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(ZHURNAL PRIKLADNOI KHIMII)

IN ENGLISH TRANSLATION

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THEORY OF THE OXIDATION OF SULFITE-BISULFITE SOLUTIONS

B. A. Chertkov

As is known, the exposure of aqueous solutions of sulfurous acid and its salts to the atmosphere or some other oxygen-containing gas results in their partial oxidation. This phenomenon has to be coped with in the preparation of the indicated solutions, and also when they are used in industrial processes. The process for the oxidation of aqueous solutions of sulfurous acid and its salts has been studied by many investigators.* A large portion of these studies was devoted to investigating the oxidation of sodium sulfite, and this compound was used as the example in evolving a general theory for the oxidation of similar solutions. The investigations revealed that the mechanism of this oxidation is considerably more complex than might be expected on the basis of the, at first glance, comparatively simple summary equation for this reaction: $O_2 + 2SO_3^{2-} \rightarrow 2SO_4^{2-}$.

Actually, the reaction with molecular oxygen and conversion of sulfite to sulfate goes through a number of intermediate compounds, whose character and the conditions for their formation are still not too clear at the present time. Another major complication here is the sensitivity of the oxidation process to the action of certain additives, capable of changing the course of the intermediate reactions and causing under some conditions an acceleration, and under other conditions, a deceleration of the over-all oxidation process. Of the earlier proposed theories offering to explain the mechanism of the intermediate reactions, and also the mechanism of the action of positive and negative catalysts, the chain theory [2] has received the widest acceptance. According to the theory, the SO_3^- ions of monothionic acid HSO_3, which at the same time could be regarded as being the radical of the sulfuric acid molecule, function as the active centers of the generated chains.

Recently Abel [1, 3] proposed a new theory for the oxidation of sulfites, offering a different mechanism for the intermediate reactions. According to Abel's theory, molecular oxygen first reacts with the dissociation products of water, leading to the formation of O_2^- and OH radicals, which then participate in the formation of the HSO_3 radical, and then the SO_4^{2-} ion.

The kinetic equations that Abel derived on the basis of this theory show that the oxidation rate of sulfite-bisulfite solutions is directly proportional to the concentration of the HSO_3^- ion and inversely proportional to the square root of the H^+-ion concentration. This general conclusion is found to be in agreement with the experimental results obtained by some investigators when they oxidized pure sulfite solutions under laboratory conditions, and, in particular, it is in agreement with our data on the oxidation rate of pure ammonium sulfite-bisulfite [4].

However, the existing theories, including the Abel theory, cannot give a satisfactory explanation for the sharp fluctuations that are observed in the degree of oxidation when going to industrial conditions, where concentrated ammonium sulfite-bisulfite solutions, contaminated with different impurities, are used. Thus, for example, it was observed that the presence of thiosulfate as impurity in the ammonium sulfite-bisulfite solution is capable of causing a substantial increase in the oxidation rate of the solution, at times the increase being several times the rate observed in the absence of the thiosulfate [4]. In this case the usual oxidation of the sulfite-bisulfite by the above-given Abel scheme is supplemented by a much more powerful oxidation, proceeding by some other scheme in which the thiosulfate ion functions as a catalyst. Since thiosulfate is an unavoidable impurity in commercial sulfite-bisulfite solutions, it is very important to give, proceeding from existing theoretical concepts, a correct interpretation of the reasons for its exerting such an influence on the oxidation process.

*A more complete summary of the work done up to 1951 is to be found in [1].

As is known, the presence of thiosulfate as impurity in sulfite-bisulfite solutions is mainly due to the spontaneous decomposition of the thermodynamically unstable bisulfite.* According to Foerster [5], the initial stage of the spontaneous decomposition of bisulfite proceeds according to the following scheme:

$$4HSO_3^- \longrightarrow S_3O_6^{2-} + SO_4^{2-} + 2H_2O; \tag{2}$$

the trithionate formed here immediately suffers hydrolysis and converts to thiosulfate and sulfate

$$S_3O_6^{2-} + H_2O \longrightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+. \tag{3}$$

The same as is true for other thiono compounds, the chemical structure of the thiosulfate and trithionate molecules is easily established if we resort to the polythionate theory of D. I. Mendeleev, which has found confirmation in a number of recent studies [6]. According to this theory, thionic acids represent sulfonic acids that are formed by replacing the H atoms in hydrogen sulfide or polysulfide by the sulfo group, i.e., by the HSO_3 radical. Thus, the structure of thiosulfate or thiosulfuric acid should correspond to the formula $H \cdot S \cdot (HSO_3)$, trithionic acid to $(HSO_3)S(HSO_3)$, and tetrathionic acid to $(HSO_3)S_2(HSO_3)$.

In this connection it could be expected that the HSO_3 radical, formed in the sulfite-bisulfite solution, will react with the thiosulfate present in the solution and will convert it to trithionate in accordance with the following typical scheme:

$$\underset{\text{Thiosulfate}}{HSO_3 + OH + H \cdot S \cdot HSO_3} \rightarrow \underset{\text{Trithionate}}{S(HSO_3)_2} + H_2O. \tag{4}$$

Because of hydrolysis, the trithionate will be continuously transformed according to reaction (3) into starting thiosulfate and sulfate. Then the thiosulfate can react anew with the HSO_3 radical, etc.

In the presence of thiosulfate, the main reactions of the oxidation process can be represented as follows (similar equations can also be written for the oxidation of bisulfite):

$$SO_3^{2-} + O_2^- + S_2O_3^{2-} + 3H^+ \longrightarrow S_3O_6^{2-} + OH + H_2O \tag{5}$$

and

$$SO_3^{2-} + 2OH + S_2O_3^{2-} + 2H^+ \longrightarrow S_3O_6^{2-} + 2H_2O \tag{6}$$

After the formed trithionate has undergone hydrolysis according to equation (3) the liberated thiosulfate will again take part in reactions (5) and (6), etc. The frequency with which these cycles are repeated will determine that acceleration in the over-all process of oxidizing sulfite-bisulfite solution that is due to the presence of thiosulfate in the solution.

The catalytic action exerted by thiosulfate is linked with its participation in the continuous thiosulfate-trithionate conversion, facilitating the more rapid oxidation of the sulfite-bisulfite solution.

The theoretical possibility of reactions (5) and (6) going can be confirmed by thermodynamic calculation. Thus, assuming from the data given in [7] that the free energies of formation of the ions and radicals taking part in these reactions are equal to (in kcal): $SO_3^{2-} = -116.1$, $O_2^- = +13$, $S_2O_3^{2-} = -124$, $H^+ = 0$, $S_3O_6^{2-} = -229$, $OH = +8.53$, $H_2O = -56.69$, $HSO_3^- = -126$, it becomes possible to calculate that the total change in the free energy ΔF° according to equation (5) is -50.1 kcal, and according to equation (6) it is -119.3 kcal. If it is bisulfite ion that takes part in reactions (5) and (6), and not sulfite ion, then ΔF° is, respectively, -40.2 kcal and -109.3 kcal. The high negative values for the change in the free energy serve as evidence that it is theoretically possible for these reactions to go in the indicated directions.

*At times it is possible for thiosulfate to be formed as the result of impurities of a reducing nature, for example H_2S, being absorbed from the gas. The reaction can be depicted by the following typical scheme:

$$SO_3^{2-} + HSO_3^- + H_2S \longrightarrow 1.5\ S_2O_3^{2-} + 1.5\ H_2O. \tag{1}$$

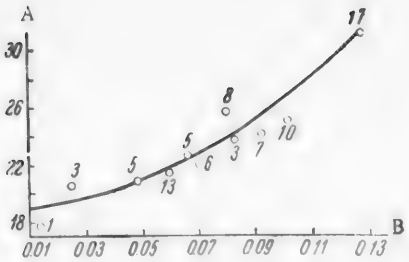

Fig. 1. Oxidation rate of ammonium sulfite-bisulfite in cyclic process for extraction of SO_2 from gases with a variable content of thionates in the solution. A) Rate of ammonium sulfate formation (in mole/hr); B) amount of $S_2O_3^{2-} + S_3O_6^{2-}$ (in mole/liter).

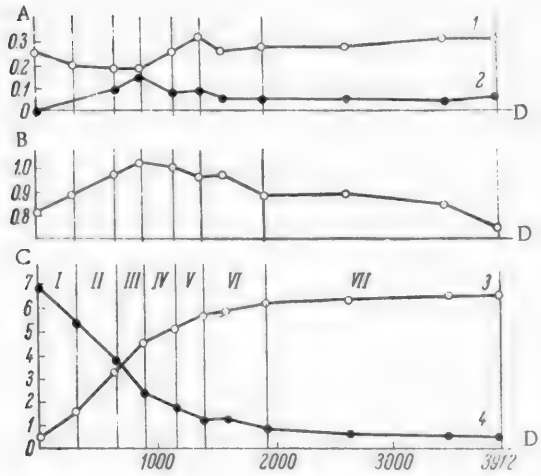

Fig. 2. Oxidation rate and change in composition of ammonium sulfite-bisulfite solution when exposed to air in the presence of 0.25 mole/liter of thiosulfate. $NH_{3\,total}$ = 7.32 moles/liter, $S/C_{initial}$ = 0.81, temperature 20 - 22°. A) Amount (in mole/liter) of $(NH_4)_2S_2O_3$ (1) and of $(NH_4)_2S_3O_6$ (2); B) S/C ratio; C) amount (in mole/liter) of ammonia as ammonium sulfate (3) and as ammonium bisulfate (4); D) time (in hr). Rate of oxygen absorption g_{O_2} (in g/sq m/hr) in different periods: I) 3.19, II) 5.51, III) 4.53, IV) 2.30, V) 1.74, VI) 0.89, VII) 0.11.

The validity of the explanation given above for the course of the oxidation process in the presence of thiosulfate can also be confirmed by existing experimental data.

In Fig. 1 we give some data on the effect exerted by the total content of thiosulfate and trithionate in the operating solution on the oxidation rate of the latter, which data were obtained in a study of the cyclic ammoniacal extraction of SO_2 from gases in an experimental unit [8]. The absorbent was an ammonium sulfite-bisulfite solution with a total concentration of 5—7 moles/liter.

As can be seen from Fig. 1, the rate with which the solution oxidizes begins to increase even in the presence of trace amounts of thionates. The character of the obtained curve indicates that it is possible to obtain an even sharper rise in the oxidation rate by increasing the concentration of thionates in the solution further.

In our previous paper [4] we gave a graph (Fig. 2), showing both the oxidation rate and the change in the composition of pure ammonium sulfite-bisulfite solution when exposed to the air.

In the present paper we have plotted in Fig. 2 the oxidation rate of the same solution, except that 0.25 mole/liter of thiosulfate had been added to it in advance. The addition of the thiosulfate caused a very sharp increase in the oxidation rate, exceeding by a matter of 3—4 times the oxidation rate in the corresponding periods for the solution without the addition of thiosulfate.

Together with this, the data plotted in Fig. 2 show that, as has been discussed above, there is actually interconversion between thiosulfate and trithionate. Evidence of this is the decrease in the thiosulfate concentration with a simultaneous increase in the trithionate concentration that is observed at the start. The presence of interconversion between thiosulfate and trithionate is shown even more clearly in Fig. 4 of [4], where we have plotted the oxidation rate of a solution differing from the above only in that it has a higher $S/C_{initial}$ ratio. In view of the fact that the S/C ratio soon exceeded one,* the spontaneous decomposition of the thermodynamically unstable bisulfite proceeded much more rapidly here than in previous cases, which points to the substantial increase in the total concentration of thionates in the solution.

Also of interest are the data obtained by us using technical p-phenylenediamine as an inhibitor to retard the oxidation of pure ammonium sulfite-bisulfite solutions, which matter has been discussed in a previous paper [9]. In Fig. 2 of this paper [9] we have shown the effect of adding different amounts of inhibitor on the oxidation

*As evidenced by the appearance of free sulfuric acid above the bisulfite and a corresponding decrease in the pH of the solution. For a characterization of the S/C ratios see [4].

of a solution in which the concentration of thionates is equal to zero. In Fig. 4 of [9] we have shown the effect of adding inhibitor on the oxidation of a solution differing from the preceding only in that 0.25 mole/liter of thiosulfate was added to it. The retarding effect of the inhibitor proved to be very great in both cases, despite the fact that the oxidation rate of the original solution increased here by a matter of approximately 3 times.

As a result, the effect of the inhibitor is not limited only to retarding the direct oxidation of the sulfite-bisulfite by molecular oxygen, but it also paralyzes the catalytic activity of the thiosulfate that is unavoidably present in commercial sulfite-bisulfite solutions. This fact undoubtedly possesses great practical importance for many processes where oxidation of sulfite-bisulfite is undesirable. Together with this, it serves as indirect proof of the validity of our explanation for the catalytic role played by thiosulfate in the general mechanism for the oxidation of sulfite-bisulfite solutions.

SUMMARY

The existing theory for the oxidation of pure dilute sulfite-bisulfite solutions is inadequate for explaining the sharp increase in the oxidation rate observed for concentrated commercial sulfite-bisulfite solutions, unavoidably containing thiosulfate as impurity. We have given an explanation for the catalytic role played by thiosulfate in the general mechanism for the oxidation of sulfite-bisulfite solutions, which explanation is supported by the experimental results obtained for the case of the oxidation of ammonium sulfite-bisulfite.

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RULES FOR THE FORMATION OF SULFIDES AND OXIDES OF METALS IN THE THERMOCHEMICAL DECOMPOSITION OF THE SULFATES OF MANGANESE AND IRON

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The thermochemical decomposition of sulfates finds extensive use in nonferrous metallurgy and in various chemical industries [1-4]. The thermochemical transformation of sulfates under reducing conditions permits obtaining, both as intermediate and as end reaction products, the corresponding oxides, sulfides, sulfites, carbonates and thiosulfates, while various sulfur-containing compounds may be obtained as the gaseous products. The reductive roasting of sulfates is a very complex process, and consequently the composition of the reaction products depends on a large number of factors.

In this paper our purpose was to determine the principal factors affecting the formation of metal sulfides and oxides when sulfates are reduced with carbon. For this we studied both the qualitative and the quantitative compositions of the thermochemical decomposition products of sulfates as a function of the temperature, the amount of carbon in the mixture, the addition of certain metal oxides, the composition of the gas phase, and the physicochemical properties of the substances taking part in the reaction.

As the principal subjects of study we selected the sulfates of iron and manganese. In addition, we investigated the reduction of the sulfates of zinc, magnesium and calcium with carbon.

EXPERIMENTAL

The carefully dehydrated sulfates, as well as their mixtures with carbon and different additives, were roasted in a laboratory tube furnace in a stream of dry, pure argon, and in some cases, discussed separately in the text, in a stream of argon containing 7.5% SO_2. The gaseous sulfur-containing products obtained from the roasting, and also the sulfate sulfur, were analyzed using previously described methods [4, 5]. The qualitative and quantitative compositions of the products from the roasting were determined by x-ray and chemical analysis techniques. It was found that the products obtained from the reductive roasting of the sulfates of magnesium, zinc, manganese and calcium contain various amounts of the corresponding sulfides. The products from the reductive roasting of ferrous sulfate were found to contain, along with a certain amount of iron sulfide, substances of the pyrrhotite type. The sulfur of the sulfates soluble in hydrochloric acid was determined by the Foerster and Kubel method [6], while the sulfur of the pyrrhotites was determined by the Eschka* method. The $FeSO_4$, $MnSO_4$, $MgSO_4$, $CaSO_4$, and $ZnSO_4$ used in our experiments were of pharmacopoeia grade, and we also used the dry, pure oxides of manganese, zinc, aluminum, magnesium and calcium. We took birch charcoal (10% volatiles) as the carbon-containing material. The oxygen content in the argon did not exceed 0.03%. The roasting products were quenched under conditions that avoided oxidation of the sulfides during cooling. The weight of the samples taken for operation ranged from 1.0 to 1.5 g. The carbon content in the starting mixture was varied from 0.0 to 32.5%. The time of experiment was equal to 15 min in all cases.

The principal results of the experiments are given in Tables 1-6.

* Transliteration from the Russian.

TABLE 1

Degree of Thermochemical Conversion of Ferrous Sulfate as a Function of the Temperature and Amount of Carbon in the Mixture

Amount of carbon in mixture (in %)	Degree of $FeSO_4$ conversion (in %)						
	450°	500°	550°	600°	650°	700°	750°
0.0	0.0	0.8	4.7	25.4	66.6	92.7	99.6
5.0	0.9	7.2	49.6	84.3	95.9	98.2	99.8
10.0	2.3	15.1	70.0	93.7	98.8	99.1	99.4
20.0	4.6	21.9	75.1	96.6	99.3	99.4	99.7

TABLE 2

Thermochemical Decomposition of Ferrous Sulfate. Degree of Conversion of Sulfate Sulfur as a Function of the Temperature and Amount of Carbon in the Mixture

Amount of carbon in mixture (in %)	Degree of conversion of sulfate sulfur (in %)						
	750°		800°		850°		900°
	sulfide	pyrrhotite	sulfide	pyrrhotite	sulfide	pyrrhotite	sulfide
10.0	0.8	3.5	2.1	4.8	6.7	7.2	11.4
20.0	1.3	6.7	8.4	5.6	10.3	15.1	23.1
30.0	3.4	10.6	12.1	24.3	21.2	—	—

The thermal decomposition of ferrous sulfate in the absence of reducing agent can be observed at 500-550°. In the temperature range up to 675° the process takes place in the kinetic region, and at temperatures above 725° the process takes place in the diffusion region (Table 1). At temperatures exceeding 750° the decomposition of $FeSO_4$ proceeds very rapidly and to completion. The end solid product of roasting under these conditions is chiefly Fe_2O_3. The gas phase is composed of a mixture of SO_2 and SO_3. The absolute amount of sulfur trioxide in the gas phase reaches a maximum at 700-750°, after which it decreases.

The thermal decomposition of manganese sulfate had been investigated by us earlier [5]. It proved that the decomposition of $MnSO_4$ can be observed at 750°, i.e., some 200° above the corresponding temperature for the decomposition of $FeSO_4$. In addition it was established, maintaining the other conditions constant, that the investigated sulfates can be arranged in the following order of decreasing degree of thermal decomposition:

$$FeSO_4 > ZnSO_4 > MnSO_4 > MgSO_4 > CaSO_4. \quad (1)$$

Further, we have given in Tables 1, 2, 4 and 6 the results of studying the degree of decomposition and the composition of the products obtained when the above-indicated sulfates are roasted in the presence of carbon.

It proved that the end solid products from the reduction of the sulfates of iron, zinc, manganese, magnesium and calcium with carbon are the corresponding oxides and sulfides. The relative amounts of these substances in the roasting products can vary within wide limits, depending on the physicochemical properties of the components taking part in the reaction, and also on the conditions employed.

For a more detailed discussion of the factors determining the composition of the end reduction products of sulfates we will turn to the results given in Tables 1, 2 and 4.

TABLE 3

Thermochemical Decomposition of Ferrous Sulfate. Degree of Conversion of Sulfate Sulfur to Sulfide Sulfur as a Function of the Temperature and Amount of Additive

Oxide added	Degree of conversion of sulfate sulfur to the sulfide (%)							
	700°		750°		800°		850°	
	amount of carbon in mixture (in %)							
	10	20	10	20	10	20	10	20
ZnO	1.2	1.8	2.5	2.7	3.0	4.3	—	11.6
Mn_2O_3	3.9	6.1	8.2	15.4	19.3	29.7	21.0	37.8

TABLE 4

Degree of Thermochemical Conversion of Manganese Sulfate as a Function of the Temperature and Amount of Carbon in the Mixture. 1) Total degree of $MnSO_4$ conversion (in %); 2) degree of conversion of sulfate sulfur to sulfide sulfur (in %)

Amount of carbon in mixture (in %)	Degree of $MnSO_4$ conversion (in %)									
	650°		700°		750°		800°		850°	
	1	2	1	2	1	2	1	2	1	2
13.8	8.2	0.0	33.7	0.0	79.1	0.4	93.2	5.8	97.7	16.5
19.3	17.8	0.0	65.6	1.0	91.1	5.3	96.1	12.5	98.6	22.6
32.5	20.4	0.8	72.2	3.2	94.6	15.4	97.9	29.7	99.0	40.8

The data in Tables 1 and 4 permit concluding that the addition of carbon to the batch greatly intensifies the thermochemical decomposition of the sulfates of iron and manganese. The thermochemical decomposition of these sulfates in the presence of carbon can be observed at 450° ($FeSO_4$) and at 650° ($MnSO_4$). In other words, the addition of carbon lowers the temperature of noticeable decomposition of the indicated sulfates by approximately 100°. Increasing the amount of added carbon increases the degree of thermochemical decomposition suffered by the sulfates of iron and manganese. This circumstance is especially obvious at temperatures where the process takes place in both the kinetic and transition regions. For the case of reducing $FeSO_4$ with carbon the transition region is limited to temperatures up to 625°, while for the case of $MnSO_4$ reduction this region goes up to temperatures of 750 - 775° (Tables 1 and 4). In the diffusion region a substantial increase in the amount of added carbon above 5 - 10% is practically without effect on the degree of thermochemical decomposition suffered by the sulfates of iron and manganese.

It was established that the amount of carbon in the starting mixture affects both the decomposition rate and the composition of the products obtained in the reductive roasting.

When the amount of carbon in the starting mixture does not exceed 5-10% the principal solid products of the thermochemical decomposition of the sulfates of iron and manganese are the corresponding oxides. Here the sulfur in the gaseous roasting products is found mainly as SO_2. On increasing the amount of carbon in the starting mixture above 10-15% it is possible for the end reduction products of $FeSO_4$ and $MnSO_4$ to also contain the corresponding sulfides. In an adequate reducing atmosphere the formation of pyrrhotites, and also of iron and manganese sulfides, proceeds at a noticeable rate at temperatures above 750° (Tables 2 and 4).

TABLE 5

Thermochemical Decomposition of Manganese Sulfate. Degree of Conversion of Sulfate Sulfur to Sulfide Sulfur as a Function of the Temperature and Amount of Additive (Amount of carbon in mixture = 24.2%)

	Degree of conversion of sulfate sulfur to the sulfide (in %)				
	700°	750°	800°	850°	900°
Without additive	1.8	10.3	21.5	31.6	35.5
Without additive*	2.0	31.1	59.1	82.0	87.5
Additive:					
CaO	8.9	27.0	37.5	60.1	71.7
Mn_2O_3	26.7	57.4	64.1	70.8	72.3

*In a stream of argon containing 7.5% SO_2.

TABLE 6

Thermochemical Decomposition of Magnesium, Iron, Manganese, Zinc and Calcium Sulfates. Degree of Conversion of Sulfate Sulfur to the Sulfide as a Function of the Temperature (Amount of carbon in mixture = 28.0%)

Sulfate	Degree of conversion of sulfate sulfur to the sulfide (in %)					
	700°	750°	800°	850°	900°	950°
$MgSO_4$	0.1	0.1	0.2	0.1	0.3	0.3
$FeSO_4$	0.4	2.5	10.8	19.3	25.6	—
$MnSO_4$	2.2	12.1	26.7	37.5	39.0	48.8
$ZnSO_4$	10.4	22.3	34.4	43.3	50.1	53.3
$CaSO_4$	0.0	1.1	3.6	15.2	50.0	87.7

Consequently, it may be assumed that the composition of the solid products of the reduction of ferrous sulfate, and especially of manganese sulfate, can be varied within quite wide limits, depending on the reaction conditions employed.

The temperature should not exceed 700-750°, and the amount of carbon in the batch should be minimum if it is desired to obtain the oxides of the metals as the chief products of reductive roasting Conversely, to obtain large amounts of sulfide sulfur in the roasting products it is necessary to run the process at a higher temperature and with a larger amount of carbon in the starting batch.

It must be assumed that the degree of conversion to sulfide will depend on the physicochemical properties of the components taking part in the reaction, and also on the amount of sulfur dioxide in the gas phase. The latter is illustrated by the data given in Table 5, from which it follows that increasing the amount of SO_2 in the gas phase during the reduction of $MnSO_4$ leads to a substantial increase in the amount of manganese sulfide in the products from the roasting.

The results given in Table 6 permit arriving at a conclusion as to the effect exerted by the physicochemical properties of both the sulfates being reduced and the substances formed from them on the amount of sulfides in the roasting products.

It can be seen that comparatively small amounts of sulfides are formed when the sulfates of magnesium and iron are reduced under the same conditions. Conversely, the reduction of the sulfates of zinc, calcium and manganese under certain conditions can lead to the formation of quite substantial amounts of sulfides (Table 6).

The data presented above indicate that a direct relationship fails to exist between the equilibrium dissociation pressure, or the decomposition rate of the sulfate and the extent to which sulfide is formed in the reductive roasting process. As a matter of fact, reduction of the more heat stable $MgSO_4$ yields a much smaller amount of sulfide than does the reduction of the less heat stable $ZnSO_4$, while the reverse situation is observed for the sulfates of calcium and iron. The thermally more stable $CaSO_4$ is reduced mainly to the sulfide, while the thermally less stable $FeSO_4$ is reduced mainly to the corresponding metal oxides (Table 6).

Consequently, the conclusion arises that the amount of sulfides formed in the reduction of sulfates is much more dependent on the extent to which the corresponding metal oxides are converted to sulfides by the sulfur-containing compounds present in the roasting products.

As had been shown earlier [5], the ease with which certain metal oxides are converted under reducing conditions to the corresponding sulfides by the gaseous sulfur-containing products can be depicted in the following order of increasing degree of conversion:

$$Al_2O_3 < MgO < FeO < ZnO \cong MnO.$$

An examination of this series clearly reveals why, based on the increasing ease with which the sulfides are formed in the reductive roasting process, it is possible to arrange all of the studied sulfates in the following sequence:

$$MgSO_4 < FeSO_4 < ZnSO_4 \cong MnSO_4.$$

Reduction of the sulfates found on the left side of this series yields mainly metal oxides; depending on the reaction conditions employed, reduction of the sulfates found on the right side of the series can lead to the forma- of either oxides or sulfides, or of both simultaneously.

The results obtained in studying the influence of additives also indicates that the sulfidation process plays an important role in the reductive roasting of sulfates (Tables 3 and 5).

It was proved that when various metal oxides were added to mixtures composed of sulfate and carbon, the former in a number of cases were converted to sulfide by the sulfur-containing products formed in the reduction of the sulfate. It was established that the sulfates of iron and manganese practically do not sulfidize the oxides of aluminum and magnesium, but at the same time, under certain conditions, they do sulfidize to a substantial degree the oxides of zinc, manganese and calcium (Tables 3 and 5). Thus it can be seen that the sulfidation of these oxides by the sulfates of iron and manganese obeys the same rules as were found for the sulfidation of metal oxides by sulfur dioxide in a reducing atmosphere [5]. These data make it possible to judge the behavior of various impurities in the reduction of sulfates.

SUMMARY

The obtained experimental material made it possible to disclose the principal factors influencing the composition of the solid products obtained in the reduction of sulfates by carbon.

It was established that both the rate and completeness with which sulfides are formed when sulfates are reduced in the presence of carbon depend on the temperature, the amount of reducing agent in the mixture, the extent to which the formed oxides are converted to sulfides by the sulfur-containing reduction products, and the concentration of both the oxygen and the sulfur dioxide in the gas phase.

Knowing this information, it becomes possible, by intelligently choosing the proper process conditions, to vary not only the rate of the process, but also the composition of the products obtained in the reductive roasting of sulfates.

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AUTOMATIC REGULATION OF PROCESS FOR PRECIPITATION OF BASIC NICKEL CARBONATE BASED ON THE pH OF THE MEDIUM IN THE SYSTEM $Ni(NO_3)_2 - Na_2CO_3 - H_2O$•

I. M. Vasserman, E. A. Fomina and Kh. Z. Brainina

The introduction of a complex automatic regulation of several parameters in chemical production in order to obtain a product with given properties requires making an exhaustive research study. Special attention should be given here to determining if it is possible to automatically regulate the process within the limits permissible for change in the parameters under technological conditions.

Such a case is the preparation of basic nickel carbonate, which serves as the raw material for the production of nickelous and nickelic oxide. The latter compounds find extensive use in the manufacture of semiconductor magnetic materials (ferrites), radioceramic articles and catalysts. Basic nickel carbonate is obtained by chemical precipitation when a soluble nickel salt is reacted with an alkali metal carbonate, for example, by precipitation in the system $Ni(NO_3)_2-Na_2CO_3-H_2O$. The obtained precipitate should not retain impurities tenaciously and should permit their removal by washing with water, it should filter easily, and it should have a definite structure and certain other properties. The parameters of the precipitation process are the pH of the medium, temperature, relative supersaturation, time of precipitation, etc. The necessary constancy of the structure and properties of the precipitate can be achieved only by a careful observance of the precipitation conditions. A simultaneous regulation of several parameters of the process manually is extremely difficult and does not achieve the goal. In this case it is necessary to go to a complex automatic regulation of the process.

If an automatic regulation of the temperature, relative supersaturation, time of precipitation and other parameters is possible and does not cause special difficulties, still an automatic regulation of the precipitation process based on the pH does not prove to be possible in all cases. This is explained by a coupling of the properties inherent to the pH as a parameter of the precipitation process: 1) the presence of buffer phenomena, which can be expressed by the index $\sigma = \frac{\Delta pH}{\Delta \Phi}$, characterizing the resistance shown by the medium to change in the pH when the precipitant is added or when the medium is diluted with water; 2) complication of the precipitation process by secondary phenomena; and 3) a nonlinear (logarithmic) relation between the values of the pH and the concentrations of H^+ ions in the solution, as a result of which a proportionality fails to exist between the change in the pH and the amount of precipitant added to the material being precipitated. This proportionality is possible when small changes in the amount of added precipitant correspond to rapid and substantial changes in the pH of the solution and when they are reproducible.

For this reason, in determining whether it is possible to regulate the precipitation process by the pH it is necessary to make a careful study of the course of the chemical precipitation reaction and its dependence on the pH. It is convenient to make such a study employing the potentiometic titration curve of the precipitation process [1-3].

•Communication III in a series of papers on the technology of isolating substances from solution by the method of chemical precipitation.

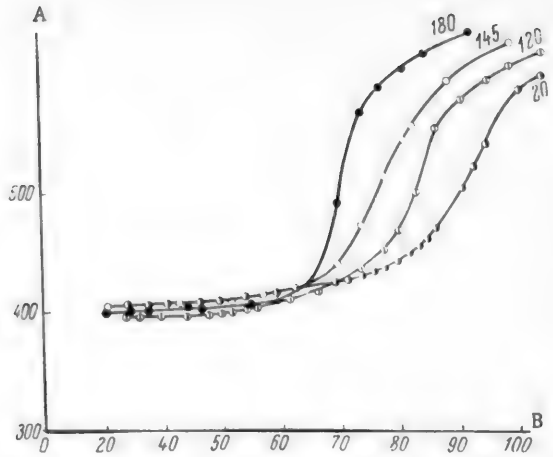

Fig. 1. Potentiometric titration of nickel nitrate solution with sodium carbonate. A) Potential of antimony electrode (in mv); B) stoichiometric ratio $\frac{Na_2CO_3}{Ni(NO_3)_2}$ (in %). The numbers on the curves designate the time of precipitation (in min).

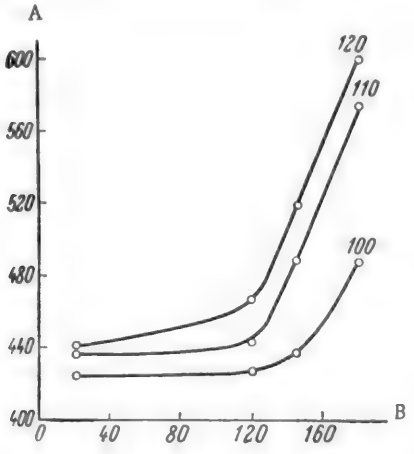

Fig. 2. Dependence of the electrode potential on the time of precipitation and the stoichiometric ratio $\frac{Na_2CO_3}{Ni(NO_3)_2}$. A) Potential of antimony electrode (in mv); B) time of precipitation (in min). The numbers on the curves designate the stoichiometric ratio $\frac{Na_2CO_3}{Ni(NO_3)_2}$ (in %).

EXPERIMENTAL

The experimental technique was described earlier [4]. Based on a study of the technological chemical precipitation of basic nickel carbonate, we adopted a temperature of 90° for the process. The length of the precipitation process was varied (20, 120, 145 and 180 minutes). In each experiment we charged 25 ml of 0.1 M $Ni(NO_3)_2 \cdot 6H_2O$ in 400 ml of water into the reaction vessel, and after heating in the thermostat sodium carbonate solution (0.1 M) was added gradually from a buret to the vessel.

We used the antimony–saturated calomel electrode pair as the measuring device. The emf of this electrode pair was measured at 90°. Automatic regulation of the process in the technological experiments was based directly on the emf reading of the electrode pair. The experimental data are given in the table and plotted in Figs. 1-6. From the curves in Fig. 1, where the potential values of the antimony electrode are plotted as a function of the amount of sodium carbonate added to the system, it can be seen that the process of chemical precipitation in the system $Ni(NO_3)_2-Na_2CO_3-H_2O$ is characterized not by one potentiometric titration curve, as is customary, but by a set of curves having a different rise. The shape of the curves in Figs. 1 and 2 indicates that at a constant stoichiometric $\frac{Na_2CO_3}{Ni(NO_3)_2}$ ratio, achieved by the addition of precipitant (sodium carbonate), the pH of the system proves to be different, depending on the time of the precipitation process. An automatic regulation of the process based on the pH is impossible in such a system. To regulate the system it is necessary to have a well-defined relationship between the indicated values. With fixed values for the time of the precipitation process, the temperature, and the concentration of the reacting components, the potentiometric titration curve becomes well-defined.

Based on a technological study of the process we selected the following fixed values for the parameters: temperature 90°; time of process 120 min; concentration 0.1 M. Here the process of precipitation in the system $Ni(NO_3)_2-Na_2CO_3-H_2O$ is described by the curve shown in Fig. 3. Analysis of this curve reveals that it has two pH regions. One is the region of buffer phenomena in the pH range 6.7-7.9, where large amounts of added precipitant cause little change in the pH. The other is the region of a rising curve in the pH range 7.9-10, where a small change in the amount of precipitant added corresponds to a sharp change in the pH. The presence of the second region on the curve is evidence that it is possible to automatically regulate the precipitation process in the system $Ni(NO_3)_2-Na_2CO_3-H_2O$ by the pH. The range of automatic regulation of the pH can be judged from the value of the buffer index σ. The value of $\sigma = \frac{\Delta pH}{\Delta \varphi} \cdot 1000$ and its dependence on the pH are given in the table and plotted in Fig. 4. The greater the value of σ, the more sensitive the system is to regulation at the corresponding pH. The larger values of index σ (>500) lie in the pH range 8.1-9.6, which represents the complete pH range in which automatic regulation is possible.

Relation between Buffer Index and pH

pH of reaction medium	Amount of precipitant added (ml)	Amount of precipitant added φ (in mequiv)	ΔpH	$\Delta\varphi$	Buffer index $\frac{\Delta pH}{\Delta \varphi} \cdot 1000$
6.75	10	4.8	—	—	—
6.75	12	5.74	0	0.94	0
6.81	16	7.59	0.056	1.84	30.2
6.85	18	8.5	0.036	0.91	43.0
6.93	20	9.35	0.08	0.85	94.2
7.03	22	10.4	0.10	1.05	96.3
7.132	24	11.18	0.102	0.78	130.5
7.26	26	12.02	0.13	0.84	154.1
7.49	28	12.99	0.23	0.97	237.0
7.86	30	13.8	0.37	0.81	456.0
8.5	32	14.6	0.65	0.8	812.0
9.03	34	15.50	0.63	0.90	702.0
9.5	36	16.37	0.47	0.87	540.1
10.1	39.7	17.98	0.6	1.61	372.0
10.5	43	19.43	0.4	1.45	276.0

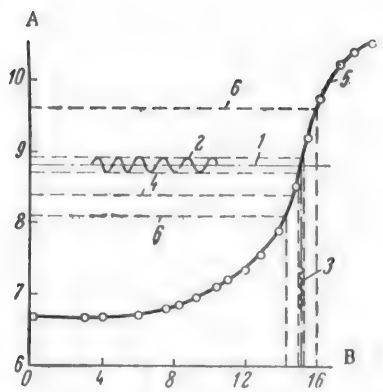

Fig. 3. Characterization of the region of automatic regulation of the process based on the value of the pH in the system $Ni(NO_3)_2$–Na_2CO_3–H_2O. A) pH; B) amount of sodium carbonate added as precipitant (in mequiv). 1) Point at which system is regulated (pH 8.8); 2) expected curve of regulation (pH 8.7-8.9); 3) expected curve for changes in the load (14.9-15.1 mequiv Na_2CO_3 per liter of solution); 4) equivalent point for the precipitation reaction (pH 8.4); 5) potentiometric titration curve in the system $Ni(NO_3)_2$–Na_2CO_3–H_2O; 6) complete range of pH values in which automatic regulation is possible.

The found region of desirable pH values is in agreement with the technological conditions used to run the precipitation process [the equivalent point of the chemical precipitation reaction is reached at a pH of 8.4 (Fig. 3)].

Consequently, a sufficiently complete precipitation will be maintained in the region of regulating the process. As can be seen from Figs 5 and 6, where the relationship between the properties of the precipitate (filtration coefficient, final volume of settled precipitate) and the pH is shown, the precipitates with the best properties are obtained at a pH above 8.2. In order to remove water-soluble anions (nitrates) adsorbed during the precipitation from the precipitate of basic nickel carbonate by washing, it is also necessary to run the precipitation at a pH above 8.4 [4]. From this it follows that the pH range (8.1-9.6), where automatic regulation of the system $Ni(NO_3)_2$–Na_2CO_3–H_2O is possible, coincides with the pH values demanded by the technological conditions of running the precipitation of basic nickel carbonate. The region of automatic regulation of the process based on the pH is characterized in Fig. 3. The equivalent point of the precipitation reaction on the potentiometric titration curve does not fix the position of the automatic regulation point. The selection of the latter depends mainly on the value of the pH at which a precipitate of basic nickel carbonate with the desired properties and composition is obtained, and it also depends on the effective value of the buffer index σ. The position of the point of regulation on the curves in Fig. 3 and 4 at pH = 8.8, with a buffer index of 710, close to its maximum value, corresponds to these conditions.

Using the glass–saturated silver chloride electrode pair as the measuring device (accuracy ± 0.1 pH), we have shown in Fig. 3 the expected curve for regulation in the pH range 8.7 -8.9 and its position in the region of possible regulation of the system. Its central position in this region and the narrow range of pH value occupied (0.2-1.5)

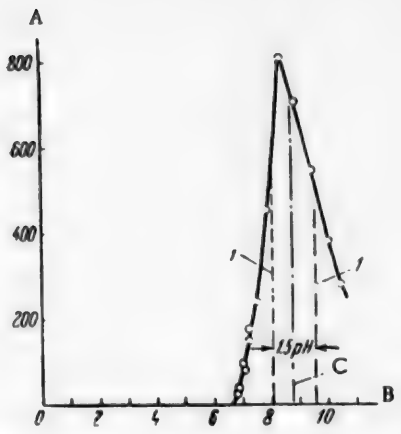

Fig. 4. Relation between the buffer index and the pH of the medium. A) Buffer index $\sigma = \frac{\Delta pH}{\Delta \varphi} \cdot 1000$; B) pH; C) point at which system is regulated. 1) Complete range of pH values in which automatic regulation is possible.

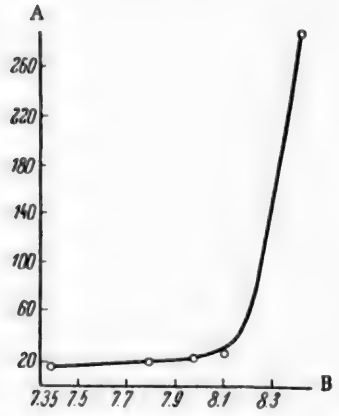

Fig. 5. Relation between the filtration coefficient of the precipitate and the pH of the medium. A) Filtration coefficient ($A \cdot 10^{-6}$) (in cm/sec); B) pH.

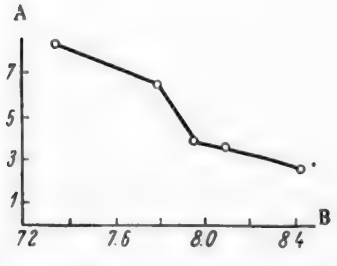

Fig. 6. Relation between final volume of settled precipitate and pH of the medium. A) Final volume of settled precipitate (cc/g of dry precipitate); B) pH of the medium.

by it both indicate favorable conditions for a stable regulation. The expected curve of changes in the load in the range 14.9-15.1 mequiv of Na_2CO_3 per liter of solution corresponds to it. The asymmetry of the point of regulation with respect to the position of the equivalent point is 0.4 pH.

DISCUSSION OF RESULTS

Based on the obtained experimental results it follows that the precipitation of basic nickel carbonate and the obtaining of a precipitate with predetermined properties can be automatically regulated by maintaining a constant pH The obtained results also indicate that precipitation in the system $Ni(NO_3)_2 - Na_2CO_3 - H_2O$ bears an anomalous character, since it is not characterized by a single potentiometric titration curve, as is usual, but by a set of curves. We had established earlier [4, 5] that the obtained precipitate of basic nickel carbonate is chemically metastable due to the precipitation process being complicated by the progress of the secondary chemical reactions: neutralization (reaction of the basic precipitate with the acid salt—$NaHCO_3$—present in the mother liquor) and hydrolysis (reaction of the basic precipitate with the water of the mother liquor). The rate with which these reactions progress under heterogeneous conditions depends on the technological factors. The thermal decomposition of sodium bicarbonate is a secondary reaction that occurs at high temperatures (>70°). The progress of these reactions causes a continuous change in the pH of the system: precipitate—solution. As a result of this, as can be seen from Figs. 1 and 2, the pH of the system can be different for the same consumption of precipitant, depending on the length of precipitation. Here the precipitate suffers "chemical aging", which leads to a change in both its physical properties and chemical composition. For this reason, in solving the problem of automatic regulation of the process, in order to obtain a precipitate with the desired properties and composition it is necessary to consider and study both the secondary reactions and the "chemical aging" of the precipitate in order to confine them to certain limits, assuring an adequate constancy of the point selected for regulation of the system. Together with time, other parameters also exert an influence on the progress of the secondary reactions and the "chemical aging" of the precipitate. Consequently, automatic regulation of the system $Ni(NO_3)_2 - Na_2CO_3 - H_2O$, based on a selected constant pH, can be accomplished only with a simultaneous regulation of all of the parameters influencing the secondary chemical reactions, i.e., with a complex automatic regulation of the precipitation process. Such regulation cannot be applied to a periodic precipitation process since its physicochemical parameters change from the start to the end of the process. However, it can be successfully applied to continuous, and with some limitations, to semicontinuous precipitation processes. Proceeding from

these considerations, we developed a semicontinuous method for the precipitation of basic nickel carbonate in which aqueous solutions of nickel nitrate and sodium carbonate were poured in a predetermined length of time into either water or mother liquor with stirring [6], and a complex automatic regulation of the process.

The results obtained in studying whether it is possible to automatically regulate the precipitation of basic nickel carbonate based on the pH are typical for obtaining the basic carbonates of other metals.

SUMMARY

1. The course of the process for the precipitation of basic nickel carbonate in the system $Ni(NO_3)_2-Na_2CO_3-H_2O$ is anomalous and is described not by one potentiometric titration curve, as is customary, but by a set of curves, the position of which under the conditions of constant solution concentrations and temperature depends mainly on the length of precipitation. The indicated set of curves exists because of the progress of secondary chemical reactions in the system $Ni(NO_3)_2-Na_2CO_3-H_2O$, caused by "chemical aging" of the precipitate, with a continuous change in its composition and in the pH values of the system: precipitate–solution.

2. When the parameters (temperature, concentration of the solutions, time of precipitation) exerting an effect on the secondary reactions have certain values, the potentiometric titration curve is well-defined.

3. The precipitation of basic nickel carbonate and the obtaining of a precipitate with the desired properties can be automatically regulated in the pH range 8.4-9.6 by employing a complex regulation of the parameters exerting an influence on the secondary reactions. A complex automatic regulation of the precipitation process can be employed only in continuous and semicontinuous methods.

4. The equivalence point of the precipitation reaction on the potentiometric titration curve does not fix the position of the point of automatic regulation based on the pH. Selection of the point of regulation depends on the pH at which the precipitate of basic nickel carbonate is obtained with the desired properties and composition, and it also depends on the value of the buffer index.

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CONCENTRATION BY COPRECIPITATION WITH CALCIUM CARBONATE AND DETERMINATION OF A NUMBER OF MICROELEMENTS IN NATURAL WATERS, WATER EXTRACTS AND WASTE WATERS

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Determination of the microelements in natural waters peculiar to a given region is an important problem in geological exploration. A procedure for the analysis of natural waters for microelements serving as indicators, under field conditions, assumes great importance for the further development of this new method of exploration.

A method for preliminary concentration of the microelements by coprecipitation with a collector is proposed in the present paper. Both the simplicity and rapidity of the operations make it possible to take the samples and run the concentrations while in the field. Besides determining traces of metals in natural waters, the method can also be used for analyzing the waste waters from industrial plants, both in the vicinity and at some distance from the source of contamination. The last circumstance bears special importance for the determination of trace amounts of radioactive elements, for example Sr^{90}.

Selection of collector. The coprecipitation of microelements, differing in their physicochemical properties (charge, ionic radius, presence in natural water as cation or as anion), excludes the possibility of selecting a collector that results in isomorphous coprecipitation. The collector must be of the adsorption type, sorbing microamounts of those cations and anions that obey the Paneth–Fajans rule, i.e., give difficultly soluble compounds with the ions of the precipitate. The surface of the precipitate possesses very great importance in this case, especially in the initial stage of the precipitation [1, 2]. Any precipitate unavoidably goes through a stage of colloidal dispersion, but it is important that the time of existing in the disperse state be sufficient to permit diffusion of the ions of the microelements to the surface of the precipitate. At the same time, the time of existing in the colloidally dispersed state should not be too long, since this retards separation of the precipitate.

In many cases the use of sulfide collectors complicates subsequent chemical analysis involving a colorimetric end-point. It is inconvenient to use hydroxides because of the great bulk of the precipitates and the lack of universality, especially when referring to the anions of the microcomponents. To a large degree, calcium carbonate as a collector lacks the indicated disadvantages. After a gradual coagulation, the precipitate assumes a dense form. The precipitate is readily soluble in acids. The calcium ion does not interfere with running a variety of color reactions between the microcomponents and organic reagents.

Another important advantage of the indicated collector is the fact that certain microcomponents present in natural waters as anions (MoO_4^{2-}, VO_3^-, WO_4^{2-}, NbO_3^-, TaO_3^-) form difficulty soluble compounds with the calcium ion.

Precipitation Conditions and Completeness of Coprecipitation of Microelements

The coprecipitation of individual microelements with calcium carbonate has been mentioned earlier by a number of investigators [3, 4]. However, the conditions under which the coprecipitations were run are not described.

TABLE 1

Coprecipitation of Microelements with $CaCO_3$ from One Liter of Solution

Element	Investigated concentration range (in γ)	Completeness of coprecipitation (in %)	Remarks
Cu	2—50	95—100	
Zn	5—60	93—100	
Mn	5—60	95—100	
Pb	5—50	95—100	
Ag	3—50	80—100	The coprecipitation was run in the presence of 1-5 mg Fe^{3+}. In the absence of iron the completeness of coprecipitation dropped sharply. Molybdenum was coprecipitated in two portions with a double amount of the collector.
Co	5—50	70— 80	
V	10—50	90—100	
W	5—50	90—100	
Mo	5—50	70— 80	
Nb	4—30	90—100*	
Be	3—40	95—100**	The coprecipitation was run in the presence of 5 mg Al^{3+} or 5 mg Fe^{3+}.

*The experiments on the coprecipitation of niobium with $CaCO_3$ in the absence of coagulant were run by A. D. Miller and N. A. Tyutina.

**The experiments on the coprecipitation of beryllium were run by A. D. Miller and M. S. Koshkina.

We used the following conditions in our experiments: the volume of solution taken for coprecipitation was 1 liter; each of the studied microelements was taken in amounts ranging from units to tens of γ/liter; in some of the experiments we added 0.5 g of the chlorides of Ca, Mg and Na in the molar ratio 2:2:1 to the solution; the amount of collector ($CaCO_3$) was chosen experimentally.

By running a series of experiments it was established that 0.06 g of $CaCO_3$ per liter of test solution is sufficient for the complete coprecipitation of microamounts of lead (5-50 γ/liter). The minimum amount of collector for the coprecipitation of microamounts of copper proved to be approximately 0.35 g. After this work, the amount of calcium for coprecipitation was taken equal to 10 mg-equiv, which corresponds to 0.5 g of $CaCO_3$. However, due to some solubility of the carbonate and small losses, the weight of the precipitate (when allowed to settle for 1.5 hr) was 0.40-0.44 g. In the early experiments the time of precipitation was determined by the rate of spontaneous coagulation and usually lasted for 1 to 2 hours. Here the precipitation was done in liter beakers by the technique of adding 10 ml of 1 N $CaCl_2$ solution and 15 ml of 1 N sodium carbonate solution, added in two portions 5 min apart and with vigorous stirring.

In subsequent experiments we used the technique of a forced coagulation of the precipitate, which greatly shortened the time of precipitation and made it possible to use a simple adaptation, a liter bottle with removable stoppers, for running the concentration. It is convenient to use such an apparatus, not only in geological explorations, but also in investigating the contamination of ponds of industrial waste waters located at some distance from the source of contamination.

However, the preliminary precipitation in beakers made it possible to establish the extent of coprecipitation of the discussed microelements and to disclose the role of the coagulant.

Some results on the completeness of coprecipitation with $CaCO_3$ from 1 liter of solution are given in Table 1. From the data in Table 1 it can be seen that the coprecipitation of the investigated microelements is sufficiently complete to permit making an approximate estimate of the amount (for a mineral content in the water up to 0.5 g/liter). The elements Sr, Ra, Ba, Ta (TaO_3^-), Th, Zr, Ti, and apparently, U, Hf, Sn^{IV} and Sb^{III} are also coprecipitated with approximately the same completeness, but the difficulty of making a chemical (but not spectral)

analysis of the precipitate does not permit a detailed discussion of these elements in the present paper.

The role of iron as an additive in the coprecipitation apparently consists in coagulating the fine suspension of calcium carbonate particles, which fail to settle even on long standing. It is also possible that ferric hydroxide serves as an additional collector for difficultly soluble compounds of the microelements. It is interesting to mention that the addition of iron functions to substantially increase the degree of coprecipitation of the microelements only if it is made prior to the addition of the sodium carbonate.

Next we ran some experiments on hastening the coagulation of the $CaCO_3$ precipitate. The choice of coagulants was limited to those which interfere the least with subsequent analysis or which are found in one form or another in the collector coprecipitate. Al^{3+} belongs to the first class, and Fe^{3+} to the second.

Both ions, if added after the sodium carbonate addition, greatly accelerate both the coagulation and the settling of the precipitate. Addition of the ions prior to adding the sodium carbonate also accelerates the coagulation, but to a lesser degree. The precipitates are sharply different. Whereas coagulation with aluminum yields a gelatinous precipitate, the use of iron for coagulation yields a very compact precipitate of the carbonate, having a brown color due to the coprecipitated iron.

Iron proved to be the more suitable coagulant for two reasons: first, the need of adding it in advance in the coprecipitation of V, W, Mo and Ag makes it necessary to take its presence into consideration in one way or another in subsequent analysis; second, the compact character of the precipitate when coagulation is with iron makes it possible to use a simple procedure, suitable for field work, for running the coprecipitation with calcium carbonate. In this case a standard liter bottle is used for precipitating the carbonate in the test water. After adding the reagents and stirring, a test tube is attached to the bottle through a drilled rubber stopper. Then the bottle is turned with the neck down, and the precipitate settles to the bottom of the test tube. After 20 min the bottle is tilted gently, the test tube with carbonate precipitate is "unscrewed", and the water is poured out of the bottle.

Analysis of the collector coprecipitates for the microelements present revealed that if the same quantities of reagents are used as in the slow coprecipitation (without coagulant), then only 0.30-0.33 g of the coprecipitate succeeds in settling in 20 min, and consequently the degree of coprecipitation of the microelements is somewhat low. However, if the amount of reagents is increased so that the theoretical weight of the precipitate is 1.0 g, while its actual weight is 0.65-0.70 g, then the same degree of coprecipitation is achieved as in the slow settling, and in some cases it is even higher. The data on the completeness of the coprecipitation of different microelements under various coprecipitation conditions are summarized in Table 2

As a result, it is possible to obtain just as good results in rapid coprecipitation as in slow. If the amount of collector is not increased, and instead the same amount is used as in slow coprecipitation (0.5 g), the results are still suitable for judging relative changes in the concentration.*

The coprecipitation of some of the elements was examined at high salt concentrations. Increasing the NaCl concentration in the water to 5 g/liter was without effect on the degree of coprecipitation of Pb and Cu, but it decreased the degree of coprecipitation of Zn by 15-20%. The presence of large amounts of Ca^{2+} (up to 5 g/liter) in the water was without effect on the completeness of coprecipitation (verified for Cu, Pb, Zn, Ag), but naturally the weight of precipitate increased here due to reaction of the Ca^{2+} with excess Co_3^{2-}. The presence of Mg in amounts ranging from 0.3 to 0.5 g/liter made it necessary to increase the amount of precipitant (sodium carbonate) and it also caused a slowing up of the precipitation process. For some of the elements (Cu, Pb, Mo, Ag) we determined the degree of coprecipitation in the presence of substantial amounts of magnesium (up to 1 g/liter). As could be expected, the degree of coprecipitation was not lowered.

For two of the elements, beryllium and molybdenum, we investigated the effect of a high mineral content (of the order of 20 g/liter—approximately 5 g of $MgCl_2$, 15 g of NaCl and about 1 g of $CaCl_2$) on the coprecipitation. The degree of coprecipitation shown by beryllium was not reduced. The amount of molybdenum in the

*With the exception of Mo, for which the degree of coprecipitation using 0.5 g of $CaCO_3$ is slightly low irrespective of whether the coprecipitation is rapid or slow. Reliable results are obtained for Mo when the theoretical weight of collector is 1.0 g.

TABLE 2

Completeness of Coprecipitation of Microelements (Percent Coprecipitation) as a Function of the Coprecipitation Conditions

Microelement	Slow coprecipitation in a beaker. Theoretical weight of collector 0.5 g	Rapid coprecipitation in a bottle with forced coagulation of the carbonate (coagulant Fe^{3+}). Time of precipitation, 20 minutes	
		theoretical weight of collector 0.5 g	theoretical weight of collector 1.0 g
	actual weight of collector (in g)		
	0.40—0.44	0.30—0.33	0.65—0.70
Cu	95—100	85	95—100
Zn	85— 90	60— 70	90— 95
Mn	95—100	85— 90	95—100
Pb	100	95—100	100
Ag	80—100	60— 70	85—100
Co	75— 85	75— 85	95—100
V	90—100	90— 95	95—100
W	90—100	85— 95	90—100
Mo	35— 50	35— 50	70— 80
Nb	90—100	Not determined	95—100
Be	95—100		95—100

coprecipitate was found to be one half that obtained under standard conditions, but parallel experiments in which known amounts of Mo were added to the precipitate revealed that nearly all of the molybdenum loss occurs in processing the bulky precipitate and subsequent operations.

For several elements (Cu, Zn, Pb, Mo, Ag) we investigated the effect of certain organic substances on the completeness of coprecipitation. The presence of citric and tartaric acids in amounts up to 5 g/liter is without effect on the coprecipitation of copper and lead; the presence of peat extract in amounts up to 0.5 g/liter (on the dry material) is also without effect. The coprecipitation of zinc under the same conditions is reduced by 10-15%. The coprecipitation of molybdenum and niobium was investigated at contents of citric and tartaric acids up to 1 g/liter and of peat extract up to 0.5 g/liter. A reduction in the degree of coprecipitation was not observed.

Possibility of Semiquantitative Spectral Analysis

When the coprecipitation was run in a bottle, we added 5 mg/liter of Fe^{3+} before precipitation of the calcium chloride with sodium carbonate and 2 mg/liter after the precipitation. A very important fact here is that nearly all of the iron appears in the $CaCO_3$ precipitate (95-100%). A constant amount of iron in a constant weight of the collector* might serve as an auxiliary means of analysis in the semiquantitative spectral determination of the coprecipitated microelements. Spectral analysis is an especially convenient technique when it is necessary to determine several microelements in one sample.

Chemical analysis of the collector for the controlling microelement can be run either on parallel samples or on a portion of the precipitate taken for spectral analysis. The quantitative spectrographic determination of certain microcomponents in carbonates is described in the literature [5-7].

Preparation of Test Solutions and Accelerated Coprecipitation Procedure

The $CaCl_2$ and Na_2CO_3 solutions (prepared from c. p. salts) were purified by the technique of "partial precipitation" [8]. The solutions were prepared 20% more concentrated than required. The calcium chloride

*For example, when the theoretical weight of collector is 1.0 g and the actual value is 0.65-0.70 g, the amount of iron will be $\frac{7 \times 100}{700} = 1.0\%$.

solution was partially (about 10%) precipitated with sodium carbonate, and the sodium carbonate solution in turn was partially precipitated (about 10%) with calcium chloride. After allowing to settle, the partial precipitation was repeated. The precipitates, containing the impurities, were discarded, while the decanted solutions were used for the work. $FeCl_3$ was obtained from pure iron carbonyl or else a solution of c. p. $FeCl_3$ was used.

A blank experiment for the presence of the microcomponent being determined was run on all of the test solutions. The concentration of the test solutions can be varied within wide limits. It is convenient to use 1 N $CaCl_2$ solution, 2 N sodium carbonate solution and a $FeCl_3$ solution containing 1 mg/ml Fe^{3+}.

A liter bottle with a rubber sleeve on the neck can be used for the work. The test tube for collecting the precipitate should have an internal diameter of 22-23 mm and a length of 80-90 mm. Twenty milliliters of 1 N calcium chloride solution is poured into each of these test tubes in advance. The test tubes are closed with pure stoppers and are held until the samples are taken.

The taking of the samples and their concentration is done as follows: the bottle is rinsed twice with the investigated water and is then filled up to the mark. If the water is strongly acid ($pH \leq 3$), then before coprecipitation the excess acid is neutralized with sodium carbonate to either neutral or weakly alkaline reaction to litmus, followed by immediately running the coprecipitation. The $CaCl_2$ solution is poured from the test tube into the water, 5 ml of $FeCl_3$ solution is added, the bottle is closed with a stopper, and the whole is mixed by shaking. Then the Na_2CO_3 solution (2 N) is added in three portions, shaking after each addition. The first sodium carbonate portion is 3 ml, the second is 5 ml, and the third is 6 ml.•

After adding the third portion and shaking, another 2 ml of $FeCl_3$ solution is added, the empty test tube is "screwed" into the rubber sleeve on the neck of the bottle, and the whole is shaken vigorously for 2 minutes. At the end of shaking, the bottle is inverted and allowed to stand in this position for 20 minutes, giving the precipitate a chance to collect in the test tube. At the end of 20 minutes the test tube is disconnected and closed with a stopper, keeping the precipitate until analyzed.

Chemical Analysis of the Collector

Usually the entire calcium carbonate precipitate was analyzed for only one microcomponent, except for the frequent case of the common presence of copper, zinc, and lead. In this case the analysis was run on one sample without subdividing the collector, but by the successive removal of the individual microcomponents.

Determination of copper, zinc and lead. The $CaCO_3$ precipitate was dissolved in hydrochloric acid and the solution warmed gently to remove the CO_2. The solution was then transferred to a separatory funnel, neutralized with ammonia until a permanent turbidity appeared, 10 ml of carbon tetrachloride and 2 ml of a 3% sodium diethyldithiocarbamate solution added, and the whole shaken vigorously for 2 minutes. The carbon tetrachloride layer, containing the carbamates of copper, lead and zinc (and iron), was separated. The CCl_4 was treated 4 times in a separatory funnel with 10 ml portions of 0.1 N HCl solution, shaking each time for 1 minute. The hydrochloric acid extracts were separated carefully (avoiding the foam) and combined.

We established that at this acidity the zinc extracts completely into the water layer, whereas the lead begins to be reextracted only at a 1 N HCl concentration, and goes completely into the water layer when the CCl_4 is treated with 3 N HCl solution. The copper does not reextract even with 6 N HCl solution.

Taking an aliquot of the combined 0.1 N HCl extracts, containing the zinc (or taking the entire extract if the amount of zinc is believed to be less than 5 γ), we added approximately 1-2 ml of a freshly prepared 25% ascorbic acid solution to reduce the Fe^{3+}. After shaking, the solution was transferred to a separatory funnel, where it was neutralized with ammonia (to litmus paper), then 6 ml of buffer solution with pH = 4.75 and 0.5 ml of 10% thiosulfate solution were added, and the zinc was determined colorimetrically using dithizone [9].

The CCl_4 layer, remaining after separation of the zinc, was treated 3 times with 8 ml portions of 3 N HCl solution,•• also shaking for 1 minute each time. A certain amount of iron, present in the extract, was reduced

•A large excess of sodium carbonate assures complete precipitation even with substantial amounts of CO_2 in the water.

••It is necessary to use acid that had been distilled by the "cold method" [10]. The ammonia used for the neutralization should also be distilled. If this is not done, the blank experiment correction is slightly high.

with ascorbic acid as indicated above, after which the solution was transferred to a separatory funnel, 2 drops of thymol blue was added, and the solution was neutralized with conc. ammonia until the red color changed to yellow (pH = 2.8), and then with dilute ammonia (1 : 100) dropwise until the indicator color changed to a blue-green (pH = 8.5). Then the lead was determined colorimetrically using dithizone [9].

The residual carbon tetrachloride layer, containing the copper carbamate and traces of iron (which interferes with the direct colorimetric determination of copper), was shaken for 2 minutes in a separatory funnel with 10 ml of lead acetate solution, containing 1 mg of Pb per ml, in the presence of 3 ml of buffer solution with pH = 5.6.

The iron was displaced from the carbamate by lead, after which the copper was determined colorimetrically by comparison with the standard series [9].

Determination of silver. The $CaCO_3$ precipitate was dissolved in conc. nitric acid and the solution was evaporated to dryness on a sand bath. The walls of the beaker were rinsed with ammonia and water, the solution acidified with excess nitric acid and the evaporation to dryness repeated. The dry residue was dissolved in 5-10 ml of 0.4-0.5 N nitric acid solution, free of nitrogen oxides, and the silver was determined by colorimetric titration using copper dithizonate as the reagent [9].

If the copper dithizonate is oxidized by impurities present in the coprecipitated sample, it becomes necessary to first extract the silver with strong copper dithizonate solution. The obtained solution of mixed copper and silver dithizonates in carbon tetrachloride is evaporated to dryness on the water bath, after which the dry residue is dissolved in 5-10 ml of 0.5 N HNO_3 solution, and then the silver is determined as indicated above.

Determination of manganese. The carbonate precipitate was dissolved in nitric acid, 3 ml of conc. HCl was added, and the solution was evaporated to dryness on the water bath. The dry residue was treated with 5 ml of conc. nitric acid, and the mixture was first evaporated and then gently ignited over a free flame or in a sand bath. The oxidative evaporation and ignition functioned to consume small amounts of organic substances extracted from the test waters by the carbonate precipitate and interfering with subsequent determination. After ignition, the dish was cooled, 15 ml of 2 N nitric acid solution and 2 ml of 85% phosphoric acid were added to the residue, then 0.5 g of dry sodium or potassium periodate (or paraperiodate), and, covering the dish with a watch glass, the mixture was heated to the boil. Gentle boiling was maintained for 10 minutes. After cooling, the dish contents were transferred to a test tube for colorimetering, and the determination was made by comparing with a series of standards, prepared as described by Sandell [9]. We added 2-3 mg of Fe^{3+} and 2 ml of phosphoric acid to each of the standards. Either ferric sulfate or nitrate is suitable here, but not the chloride, due to the reducing action of the chloride ion.

Determination of cobalt. The $CaCO_3$ precipitate was dissolved in hydrochloric acid and the solution was evaporated to dryness in a small pyrex beaker. The residue was dissolved in 10 ml of water with the addition of 0.5 ml HCl (1 : 1) and 0.5 ml HNO_3 (1 : 1), and the cobalt was determined using nitroso-R salt [9].

Determination of vanadium. The $CaCO_3$ precipitate was dissolved in the exact amount of hydrochloric acid solution (using litmus paper as a control, and then the acidity was raised to 0.5 N, followed by running the determination as the phosphotungstate complex [9].

Determination of molybdenum. The precipitate was dissolved in HCl, and the solution was transferred to a 100-ml separatory funnel, where 7 ml of conc. HCl was added and the whole made up to 50 ml with water. Then the molybdenum was determined as the thiocyanate complex using the procedure described by Sandell [9]. Approximately equivalent amounts of $CaCl_2$ and from 5-6 mg of Fe^{3+} were added to each of the standards.

Determination of tungsten. The $CaCO_3$ precipitate was dissolved in hydrochloric acid, 1 ml of 40% tartaric acid solution was added, the solution boiled to remove CO_2, then neutralized with NaOH solution, and, neglecting the possible formation of a small amount of precipitate, which dissolves in subsequent operations, the tungsten was determined as the thiocyanate complex [9]. Approximately equivalent amounts of $CaCl_2$ and from 5-6 mg of Fe^{3+} were added to each of the standards.

Determination of niobium. The $CaCO_3$ precipitate was dissolved in the minimum amount of conc. HCl. The obtained solution was then treated with saturated tartaric acid solution on the basis of 0.13 ml of tartaric acid solution per milliliter of original solution. The solution was transferred to a test tube with ground-glass

stopper and sufficient conc. HCl was added to make its final concentration in the solution 4 N. Then the niobium was determined using the thiocyanate extraction method [11].

Determination of beryllium. The $CaCO_3$ precipitate was dissolved in hydrochloric acid, avoiding a large excess, and, adding several drops of sodium acetate solution to neutralize the excess HCl, the iron was separated using 8-hydroxyquinoline [12]. Then having added 0.5 ml of HNO_3 and an excess of sulfuric acid for the amount of calcium present in the solution, the solution was evaporated nearly to dryness. Then dry trilon-B powder was added in an amount 5-10% greater than that required to complex the calcium, and the solution was neutralized to weakly alkaline reaction with conc. NaOH solution. The slight turbidity was removed either by flocculation or by filtration. Then the beryllium was determined using morin [13].

Very small amounts of beryllium are best determined spectrographically. If only beryllium has to be determined chemically, then it is more convenient to use 5 mg of Al^{3+}, and not iron as the additional collector. Also in this case the dry trilon B powder is added to the carbonate precipitate in an amount 5-10% greater than the stoichiometric, but only enough water is used to give a volume of about 5 ml. After heating the mixture to dissolve the $CaCO_3$ precipitate, followed by filtration of the turbidity and making the filtrate alkaline, the beryllium was determined using morin [13], having added equal amounts of calcium to the standards.

SUMMARY

1. A rapid method, convenient for operating in the field, was developed for concentrating the microelements found in natural waters by coprecipitation with calcium carbonate. The degree of extraction when the concentration is done from a liter of solution is quite complete for the investigated microelements: Cu, Zn, Pb, Mn, Ag, Co, V, W, Mo, Nb and Be (Sr, Ra, Ba, Ta, Th, Zr, Ti). The method can also be used for the concentration and subsequent determination of the microelements in waste waters and ponds, contaminated by the effluents from industrial plants and from the collector coprecipitate.

2. A new method was proposed for determining microamounts of copper, lead and zinc in one sample without using potassium cyanide, and in the presence of substantial amounts of iron. The method is based on the relative stability of the carbamates of Cu, Pb and Zn toward acids, which stability is sharply delineated when the carbamates are reextracted with different concentrations of acid from an organic solvent.

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APPLICATION OF THE THEORY OF SIMILITUDE TO A STUDY OF PROCESSES OF CHEMICAL TECHNOLOGY*

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In developing the theory of any process of chemical technology, in order to determine the optimum conditions for operation of the chemical apparatus it proves necessary to make extensive use of the study method in which theory is combined with experiment.

The theoretical method of analysis permits composing a mathematical description of the process in some form or another (in the form of differential equations, integral–differential equations, enumeration of the terms important for a given process, etc.). It is also known that only an experimental study of the problem without theoretical analysis greatly limits the usefulness of the obtained results, detracting from the work. It is for this reason that the similitude theory, together with a physicochemical analysis of the nature of technological processes, occupies a prominent place at the present time in technical investigations. In our country an especially great contribution in developing the similitude theory as the theory of experimental investigations, and primarily in developing the theory of heat modeling, was made by Academician Kirpichev [1] and his school [2-4].

Experiment reveals [5-11] that the methods of the similitude theory (analysis of connecting equations and analysis of dimensions) are highly fruitful when investigating the unit processes of chemical technology: hydraulic, heat, diffusion, and also the processes linked with chemical transformations. Nevertheless, a number of questions relating to the utilization of the similitude theory deserve an independent treatment and clarification. Some of these questions will be discussed below.

Boundary conditions. In a mathematical description of the investigated process it is necessary to give a very distinct and rigid formulation of the conditions for its progress at the boundaries of the space–time region, i.e., the boundary conditions (conditions of being synonymous) of the given problem.

We will examine this on one of the examples of mass transfer in the process of extraction in the system solid–liquid [12]. We will limit the problem by the following conditions. Let grad T = 0 and grad p = 0, i.e., thermodiffusion and mechanical effects are absent inside the solid; the rate with which the extracted substance dissolves in the solvent is much greater than the diffusion rate, i.e., the limiting rate of the process is truly diffusional.

In such a case the process of extraction inside the solid can be described by the differential equation of molecular diffusion. For the sake of simplicity we will write this equation in the classical form

$$\frac{\partial C}{\partial \tau} = D\nabla^2 C, \qquad (1)$$

*Based on material presented by the authors at the 8th Mendeleev Convention on General and Applied Chemistry (Moscow, March, 1959).

We will formulate the boundary conditions of the problem: let a) the geometric shape of the solid be a parallelepiped with the dimensions δ_1, δ_2 and δ_3; b) the time (initial) condition be at $\tau = 0$, with a random distribution of the mass

$$C_{\tau=0} = f_1(x, y, z, \delta_1, \delta_2, \delta_3). \tag{2}$$

Let $C_{\tau=0} = C_0$, i.e., in the initial moment the mass is distributed uniformly; c) the boundary condition be at $x = \delta_1$, $y = \delta_2$, $z = \delta_3$, $\tau > 0$

$$\beta \Delta C = -D \operatorname{grad} C_{\text{surface}}, \tag{3}$$

where grad $C_{surface}$ is taken at the surface itself.

Using the technique of similar transformation, we now can, without resorting to analytical integration, obtain quite easily:

$$E = f_2(Fo', Bi', \Gamma_1, \Gamma_2, \Gamma_3), \tag{4}$$

where $E = \frac{\Delta C}{\Delta C_0}$ is the concentration simplex; $\Gamma_1 = \frac{x}{\delta_1}$, $\Gamma_2 = \frac{y}{\delta_2}$, $\Gamma_3 = \frac{z}{\delta_3}$ are the geometric criteria; and Fo' and Bi' are, respectively, the diffusion criteria of Fourier and Biot, the conditional (transformed) analogs of similar heat criteria.

Thus, a solution of the boundary problem is found in the form of an implicit criterial function, describing the concentration field inside the solid body for the investigated extraction process. The form of this function can be obtained experimentally by known methods.

In the case where the function $Bi' = f_2(Re, Pr')$ holds, we obtain, for the discussed example, in general form

$$E = \varphi(Re, Fo', Pr', \Gamma_1, \Gamma_2, \Gamma_3). \tag{5}$$

As an example, illustrating the explicit form of the criterial function with respect to the kinetics of the extraction, we will present the following equation

$$E = 0.87 (Fo')^{-0.50} (Re)^{-0.335} (Pr')^{0.2} \tag{6}$$

which was derived by one of the authors of this paper jointly with Pao Chih-ch'üang [13, 14] as the result of an approximate modeling of the process.

Equation (6) describes within known limits the kinetics of the process for the extraction of food materials from soybean in batch equipment.

System of similitude criteria. Up to now there is no unity in the viewpoints regarding a rational system of similitude criteria. Many investigators prefer to introduce a constantly increasing number of new criteria of similitude, discarding earlier established criteria that had proved completely valid. To be sure, if new criteria of similitude arise as the result of a rigid mathematical analysis of the process, then the appearance of such criteria is quite in order. However, a number of investigators, striving to bring their own criteria of similitude into science, spend their time in an unjustified combining of some criteria with others, and at times in an exclusion or arbitrary replacement of "unsatisfactory" criteria. Although the similitude theory formally authorizes making any combinations with criteria, in no manner does this mean that preference must be given to any new combination. It must not be forgotten that formal operations with similitude criteria frequently lead to a clouding of the physical meaning of dimensionless groups, in view of which the theoretical analysis of the process fails badly. An arbitrary exclusion of similitude criteria is completely inadmissible. In this respect a simplification of the criterial equation must be approached only after an explicit form of the criterial function had been found (for example, when the values of both constant C and the exponents m, n... of the similitude criteria have been

established). Here it is permissible, for example, to bring into the total coefficient of the equation those complexes and simplexes that prove to be quantitatively unimportant, or to combine these criteria under one exponent, if the exponents are practically the same.

We believe that in treating experimental data it is necessary to first make use of the existing system of similitude criteria [1]. This is especially true when describing hydrodynamic and heat processes. In describing diffusion processes, use must first be made of the complete analogs of the criteria of heat similitude. Only here it is necessary to keep in mind that the classical equations for concentration diffusion [15] are not complete analogs of the corresponding equations for heat conductivity. This situation and, as a consequence of it, the lack of a complete analogy between the classical criteria of diffusion and heat similitude has already been discussed by us [16, 12].

The derivation of rational criteria of similitude for true chemical processes deserves separate consideration. Application of the similitude theory to investigating processes involving chemical transformations causes known difficulties due to the complexity of these processes (for example, their many stages, lack of knowledge regarding the mechanism of intermediate stages, etc.), and also for the reason that the course of these processes is determined not only by the rate of the chemical reactions, but also by physical conditions. However, even in this region some success has been achieved regarding the application of the similitude theory. For example, D'yakonov [11], not disclosing the micromechanism of a number of processes involving chemical transformations, generalized the empirical rules of their progress by employing a thermodynamic method and depicted the results of his generalizations in the form of criterial equations.

Nevertheless, it must be acknowledged that the successes achieved to date in the domain of modeling processes involving chemical transformations are only the initial step in developing a theory of similitude for these processes.

Analysis of processes by thermodynamic methods. In recent years the tendency has been to make more extensive use of thermodynamic methods to analyze and describe processes of chemical technology. Thus, for example, the methods of chemical thermodynamics have found reflection in the studies of D'yakonov [11] and Taganov [17]; Lykov [18] and his school [19] expand on the concepts of classical thermodynamics and apply the thermodynamic theory to irreversible processes in describing the phenomena of moisture transfer in materials with capillary pores and certain other processes.

In our opinion, the use of methods involving the thermodynamics of irreversible processes appears most promising for investigating complex interrelated processes (for example, when heat, diffusion and hydrodynamic phenomena are simultaneously present in the system). Here the most important is the Onsager method [20, 21], based on the use of nonequilibrium thermodynamic functions and reciprocal equations.

With the aid of this method we were able to give a quantitative-qualitative explanation for the absence of a complete analogy between the classical equations of diffusion and heat conductivity [16], and we also derived a number of new similitude criteria, characterizing the peculiarities of the molecular and convective (molecular molar) types of mass transfer in the system solid–liquid under nonisothermal conditions [12, 22]. We also applied this method to an analysis and description of the kinetics of mass and heat transfer for the case of extraction in the system solid–liquid [12].

We will give a brief analysis of the kinetics of mass- and heat-transfer for the indicated process. We will characterize the mechanism of the transfer for definite conditions, going from the general case to the particular. Let the rate of the first act (penetration of the extractant into the solid) be considerably faster than the total rate of the transfer process; the rate of the second act (solution and accompanying phenomena) is also incomparably faster than the total transfer rate, in which connection the second act is not accompanied by chemical reactions. In such case the rate of the process as a whole is limited by the rate of the third act (true extraction process). The given description of the process corresponds, for example, to the process for the extraction of sugar from sugar beet (here it is possible for the second act to be completely absent, since the sugar inside the sugar beet is already found in a state of solution).

If the influence of mechanical effects inside the solid is negligibly small (grad $p \to 0$), then in such case the rate of the third act is determined with sufficient accuracy by the rate of the interrelated transfer of mass and heat in the system. Here we have in mind both internal and external transfer. The motive force in such case is a function of the chemical potential and the temperature.

The mechanism of such a process, having in mind the transfer of mass, may be described by a differential equation [22] of the type

$$\frac{D\mu_1}{d\tau} = a_\mu \frac{L_{21}}{L_\mu}\left(\frac{\nabla^2 T}{T} - \frac{\nabla T \nabla T}{T^2}\right) a_\mu \nabla^2 \mu_1 - a_\mu \frac{\mu_1 - \mu_2}{T}\left(c_2 \nabla^2 T + \frac{\nabla T \nabla \mu_1}{\mu_1 - \mu_2} - c_2 \frac{\nabla T \nabla T}{T}\right), \tag{7}$$

where μ_1 and μ_2 are the chemical potentials of components 1 and 2, respectively; τ is the time of the process; a_μ is the conductivity coefficient of the chemical potential of the component; L_{21} and L_μ are rate coefficients, respectively expressing the conductivity of the mass under the conditions of a superimposed and principal effect (under the influence of heat and diffusion motion forces); T is the absolute temperature; and c_2 is the concentration of component 2.

Differential equation (7), derived on the basis of the thermodynamic relationships holding for irreversible processes, describes the change in the chemical potential of the components with time and space under definite conditions. Since in general form it does not lend itself to analytical integration, we resort to the methods of the similitude theory to solve the boundary problems. Using the method of similar transformation of Equation (7) and the boundary conditions, synonymously describing the investigated process, we obtain a system of similitude criteria, and then a functional relationship between them. For example, in solving one of such boundary problems [12] we obtained the equation

$$E_\mu = f(Fo_D,\ Pr_D,\ Re,\ K_2,\ K_5,\ K_6,\ G_1, G_2,\ G_3), \tag{8}$$

where Fo_D and Pr_D are, respectively, the diffusion criteria of Fourier and Prandtl (complete analogs of the similar criteria of heat similitude); Re is the Reynolds criterion; K_2, K_5 and K_6 are specific criteria, characterizing the intensity of the molecular and convective types of mass transfer under different conditions; G_1, G_2 and G_3 are geometric criteria; and E_μ is the simplex of the chemical potentials.

Criterial equation (8) describes within known limits the rate of the mass-transfer process when extraction (system solid–liquid) is under the conditions of nonisothermal transfer.

Procedural problem. In recent years there have appeared in the periodical literature and in individual reports so many new similitude criteria, while earlier established similitude criteria are written so differently at times, that occasionally it becomes difficult to decipher their physical meaning. This is especially true when considering the variety in the naming of the similitude criteria (for example, [8, 10, 23-25]), the manner in which they are written (for example, [5, 6, 26-28]), and the designations (for example, [28-30]).

In this connection we will cite the following five instances (see also [31]).

1. Very frequently the same criterion of similitude is given different names.

For example,

$\frac{\nu}{a} = Pr$ (Prandtl) $\qquad$ $\frac{\nu}{a} = St$ (Stanton)

$\frac{\nu}{D} = Pr_D$ (Prandtl, diffusion) $\qquad$ $\frac{\nu}{D} = Sc$ (Schmidt)

$\frac{a}{D} = Le$ (Lewis) $\qquad$ $\frac{D}{a} = Lu$ (Lykon) $\qquad$ etc.

2. Different investigators write criteria having the same name differently.

For example, $Fr = \frac{w^2}{gl}$, $Fr = \frac{gl}{w^2}$, $Fr = \frac{w}{\sqrt{gl}}$, $Ar = \frac{Re^2}{Fr} \cdot \frac{\rho - \rho_0}{\rho} = Ga \frac{\rho - \rho_0}{\rho} = \frac{gl^3}{\nu^2} \cdot \frac{\rho - \rho_0}{\rho}$,

$Ar = \beta \Delta t$, $We = \frac{w^2 l \rho}{\sigma}$, $We = \frac{\sigma}{\gamma l^2}$, $We = \frac{(\gamma - \gamma')\, l^2}{\sigma}$ etc.

When we say, for example, that in a stream of liquid in a pipe the term Re = 50,000, we have an idea of the hydrodynamic conditions of the process: we will say that turbulent conditions prevail here, that the molar mechanism of transfer plays a very important role, etc. Therefore, it becomes exceedingly difficult to judge the character of a process when decision is based on the magnitude of a criterion that is expressed by different quantitative relationships.

3. Different investigators make quite arbitrary modification of the similitude criteria. For example, to characterize the hydrodynamics of a suspended layer they write

$$Re_{M} = 900\pi \frac{\rho w l}{\mu} \cdot \frac{1}{1-\varepsilon}.$$

Here the Re criterion is actually only the dimensionless complex $\frac{\rho w l}{\mu}$ If the degree of diversity ϵ is represented as a dimensionless parameter in relative units of measurement, then the term $\frac{1}{1-\epsilon}$ being a function of the degree of diversity, can be regarded as a parametric criterion, characterizing the hydrodynamic specifications of the suspended layer, and this criterion, if it has important value, should not be included in the modified Re_M. As regards the constant term 900π, then it, like any constant, does not limit the freedom of scalar transformations and should be excluded from expression Re.

4. Frequently the names of prominent scientists, of whom science is justly proud, are adopted for completely random groups of terms. Such was the case when investigators "attached" the names of Mendeleev, Butlerov and other prominent chemists to such groups of terms as had been derived without proper theoretical analysis.

5. Extremely different designations of like similitude criteria are to be found in the original papers. For example, some authors designate the Reynolds criterion by the symbol Re, others by R, and some frequently by the letters N_{Re}; in like manner the Prandtl criterion is expressed by the symbols Pr, P and N_{Pr}; the Margulis criterion by M and N_M; and the Mach criterion also by M and N_M.

It seems quite obligatory to us to observe a uniformity in the writing of generally accepted and widely used similitude criteria. The assigning of names to similitude criteria should be done in a strictly established manner. The right to make changes in the papers of different authors should be reserved. It is necessary to adhere to single standards in designating the criteria. For example, we feel that the suggestion made by the German scientist Gröber [32] is a good one. According to Grober, as is known, similitude criteria are designated by the first two letters of the family name of those scientists whose investigations bear generally recognized importance in the particular field of study.

Since the problems that we have touched upon here regarding a standardization of similitude criteria go beyond the scope of a single country, it obviously follows that they should be discussed by an international commission of specialists.

At the present time the following should be included among the principal problems of chemical science: 1) further theoretical and experimental study of the physicochemical nature of different technological processes and an elucidation of their kinetic rules; 2) design of a theory of modeling, making it possible to reliably reproduce processes of chemical technology on an industrial scale; 3) generalization of the results of investigations for the purpose of developing a general theory for unit processes of chemical technology based on single kinetic rules.

SUMMARY

1. Application of the theory of similitude to solving the boundary problem was demonstrated on the example of mass transfer in extraction (system solid–liquid) under conditions of an isothermal diffusion rate.

2. Application of the methods of the thermodynamics of irreversible processes and of the similitude theory to an analysis of the kinetics of mass and heat transfer during extraction (system solid–liquid) was demonstrated for those cases where the gradients of the chemical potential and the temperature in the system are not equal to zero, while the effect of other motive forces can be neglected.

3. The problem of a system of similitude criteria for processes of chemical technology was discussed. Reference was made to the procedural problem associated with the naming, writing and designation of similitude criteria.

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STANDARD BINARY SYSTEMS FOR DETERMINING THE EFFICIENCY OF RECTIFICATION COLUMNS•

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Many binary systems have been proposed for determining the efficiency (number of plates) of rectification columns. Such problems as the manner in which these systems differ in the sense of being more or less suitable for determining the efficiency and whether they do or do not give the same efficiencies have not been considered in the literature up to now.

We investigated different liquid–vapor equilibria and used this data to construct the diagrams of number of plates vs. concentration for the following five binary systems, representing some of the systems most frequently used for determining the efficiency: benzene–carbon tetrachloride [1,2]; methylcyclohexane–2, 2, 4-trimethylpentane [3]; methylcyclohexane–n-heptane [4]; 1, 2-dichloroethane–benzene [5]; n-heptane–benzene [6]. The present paper is devoted to a discussion of which of these systems is best suited for determining the efficiency.

The suitability of a system for the indicated purpose depends on the following factors: the simplicity and accuracy of determining the compositions of both the liquid in the still pot and the reflux in the condenser; the magnitude of the error in the number of determined plates, fixed by the error of determining the concentrations of the components; the possibility of determining high efficiencies; the availability of the system components and the ease with which they are purified.

In the above-enumerated systems the compositions of the liquids were found from the refractive indices, in which connection the latter can be determined either very simply–using an Abbe refractometer (with an accuracy of $\pm 1 \times 10^{-4} n_D$), or in a slightly more complicated manner–by the method of differential reading on a precision refractometer (with an accuracy of $\pm 1 \times 10^{-5} n_D$) [2, 5].

In Table 1 we have given the number of plates that can be determined using the above-enumerated systems. In addition, we have given in this table the error in the number of plates, determined by the errors in determining the concentrations from the refractive indices.

In determining the efficiency of a column it is possible for the concentration of the low-boiling component in the liquid found in the still pot to be very small. In experiments (both special and random) where the concentration of the low-boiling component in the still pot was equal to tenths and even hundredths of a mole percent we obtained values for the efficiency that differed but slightly from the values obtained at moderate concentrations. For example: the system benzene–carbon tetrachloride, at a concentration of 20-6 mole % CCl_4 in the still pot, gave an efficiency of 33.0 (± 0.6) plates, while at a concentration of 0.22 mole % CCl_4 the efficiency proved to be 31 (± 1) plates.

The charge of liquid in the still pot can be any desired amount, but it should be sufficient to obtain flooding of the column at the start of experiment. Although quite rare, it is possible to find the statement in the literature, supported by experimental data, that the efficiency is lower when the amount of liquid in the still pot is small rather than large. From the theoretical standpoint this statement is incorrect; in our opinion, the reason the

• Communication XIII.

TABLE 1

Number of Plates and Error in Number of Plates, Determined by the Errors in Determining the Concentrations from the Refractive Indices (the error in reading the refractive indices is taken equal to $\pm 1 \times 10^{-4} n_D^{20}$)

Benzene-carbon tetrachloride	Benzene-carbon tetrachloride		Methylcyclohexane-2,2,4-trimethylpentane		Methylcyclohexane-n-heptane		1,2-Dichloroethane-benzene		n-Heptane-benzene	
	No. of plates	error in number of plates	No. of plates	error in number of plates	No. of plates	error in number of plates	No. of plates	error in number of plates	No. of plates	error in number of plates
0.01	0		0		0		0		0	
0.1	12	1.4	32	4	32	4	19	1.5	3.2	0.2
1	25	1.5	65	3.5	65	3.3	37	1.6	6.5	0.2
3	31.2	0.5	80.7	1.4	80.4	1.3	46.4	0.6	8.0	0.1
5	34.1	0.3	88.3	0.8	87.8	0.8	51.0	0.3	8.7	0.04
8	37.0	0.2	95.6	0.6	94.9	0.5	55.1	0.2	9.3	0.04
9	37.8	0.2	97.5	0.5	96.8	0.5	56.2	0.2	9.6	0.04
10	38.5	0.2	99.4	0.5	98.4	0.4	57.3	0.2	9.8	0.03
15	41.3	0.2	106.4	0.4	104.9	0.3	61.5	0.2	10.4	0.02
20	43.5	0.1	111.8	0.3	109.9	0.2	64.8	0.1	10.9	0.01
30	47.4	0.1	120.8	0.2	117.6	0.2	70.2	0.1	11.7	0.01
40	51.0	0.1	128.9	0.2	124.0	0.2	75.1	0.1	12.4	0.01
50	54.8	0.1	136.9	0.3	129.9	0.2	80.0	0.1	13.0	0.01
60	59.4	0.1	145.9	0.3	135.9	0.2	85.4	0.1	13.9	0.01
65	62.3	0.2	151.1	0.4	139.1	0.2	88.3	0.1	14.3	0.01
70	65.9	0.2	156.8	0.5	142.5	0.2	91.6	0.1	14.8	0.01
75	70.6	0.3	163.6	0.6	146.3	0.2	95.2	0.1	15.4	0.01
80	77.0	0.4	172.2	0.7	150.6	0.3	99.3	0.2	16.3	0.01
85	86.8	0.6	182.7	1.0	155.9	0.4	104.6	0.2	17.3	0.02
90	105.4	1.3	198.5	1.5	162.9	0.5	111.1	0.2	19.3	0.04
92	119.0	2.1	207.2	2.0	166.7	0.7	114.6	0.3	20.6	0.04
94	141	4	218.6	2.7	171.4	0.9	119.1	0.4	22.5	0.06
95	158	5	225.9	3	174.4	1.0	121.8	0.5	23.8	0.08
96	184	8	234.9	4	178.0	1.3	125.0	0.6	25.6	0.11
97	227	14	247	5	182.6	1.7	128.8	0.7	28.3	0.16
98	312	30	263	8	188.9	2.7	134.2	1.1	32	0.3
99	562	133	292	16	199.8	5	142.4	1.8	41	0.9
99.9	~4950*		389	17	235	5	166	1.5	75	9
99.99			486	—	271	—	187**	—	113	

Remarks. More detailed data on the number of plates for the systems enumerated in the table, and also the data on determining the concentrations using an Abbe refractometer, are given in [2-6].

The figures given in the table for the error in the number of plates decrease 10-fold when the method of differential reading on a precision refractometer is used to determine the concentrations.

The errors, distinguished by underlining, were obtained using the method of differential reading to determine the concentrations (the only method possible for the indicated concentrations).

*The data for constructing the diagrams of number of plates vs. concentration, given in communication II [2] for the system benzene–carbon tetrachloride, are expanded in Table 1 from 3 to 0.01 and from 99.0 to 99.9 mole %. As can be seen from the table, an enormous number of plates piles up in the interval 99.0-99.9 mole %; to obtain an accurate value requires employing an extremely laborious and detailed calculation method. We only wanted to show how sharply the number of plates increases in this interval, and consequently employed the usual calculation method, which in this case gives only approximate results.

**In exactly the same manner as for the benzene–carbon tetrachloride system, we expanded the data when compared with that given in communication V [5], on the number of plates for the system dichloroethane–benzene. In this system we have our last experimental value of α (relative volatility) at 99.5 mole %. The extrapolation of α from 99.5 to 99.99 mole % cannot be made with a high degree of certainty, and consequently the number of plates at 99.99% is indicated only approximately.

TABLE 2

Relation Between Amount of Liquid in Still Pot and Column Efficiency. System Benzene–Carbon Tetrachloride

Amount of liquid in still pot (in ml)	Number of plates
370	40.4
170	40.7
140	40.0
40	40.6

investigators were able to obtain experimental evidence in support of their statement was because they were unable to carry out the necessary flooding of the column with a small amount of liquid. In order to eliminate any doubt on this score, we determined the efficiency using different amounts of liquid in the still pot. The results are summarized in Table 2.

The experiments with 140 and 40 ml of liquid in the still pot were run as follows: 200 ml of the solution was poured into the still pot and the column was subjected to "cold" flooding [7], followed by operating it at the desired reflux intensity, after which a given amount of liquid was carefully removed from the still pot; then the column (operating under total reflux) was held until equilibrium was established, and its efficiency determined. The holdup in the column when operating at the reflux intensity used by us was 20 ml. In Table 2 we have given the amount of liquid present in the still pot at the time of removing the sample, i.e., 200 ml, the amount removed, representing discard and samples from the condenser (10 ml), and the holdup (20 ml).

As a result, in determining the efficiency it is possible to operate with a small amount of liquid, containing a very low concentration of the low-boiling component. However, this is inconvenient in practice. It is more convenient to take a moderate amount of liquid with a concentration such that when the column is in equilibrium the concentration of the low-boiling component in the still pot is of the order of 8 mole %. Under such conditions the composition of the reflux hardly changes as samples are removed from the condenser. For a column holdup up to 40 ml we charged 200 ml* of liquid into the still pot.

Table 1 gives a general picture of the number of plates needed to effect a nearly complete separation of the components of the discussed systems, and it also gives a general picture of the distribution of the number of plates according to the concentration and of the magnitude of the errors incurred in determining the number of plates. In Table 3, compiled from the data in Table 1, we have shown the efficiencies and the accuracy that derive when the liquid in the still pot contains 8 mole % of the low-boiling component. In determining the efficiency we have two sources of error in determining the concentration—that of the still pot liquor and of the reflux from the condenser. For this reason we have given two values for the error in Table 3.

Table 3 shows that the system n-heptane–benzene can be used to determine only low efficiencies. In addition, it is inconvenient to use this system for the reason that when operating with it in a column, insulated not by a vacuum jacket, but by the conventional externally heated jacket, there is much internal refluxing in the column. With a high column throughput this internal refluxing is completely without effect on the efficiency. However, if the column taken for operation has a low throughput, then internal refluxing begins to exert an effect. With a low throughput the column operates erratically and the reflux rate fluctuates; this may impair the efficiency somewhat, and with an even lower throughput the column may show either local flooding or a local Kafarov effect (optimum hydrodynamic conditions [8, 9]), which causes the efficiency to either decrease or increase.

From Table 3 it also follows that up to 80 plates the systems benzene–carbon tetrachloride, methylcyclohexane–2, 2, 4-trimethylpentane, methylcyclohexane–n-heptane and dichloroethane–benzene give the efficiency with nearly the same degree of accuracy (1.9-2.7% at 80 plates). Above 80 plates, using the Abbe refractometer ($\pm 1 \times 10^{-4} n_D$), only the methylcyclohexane–2, 2, 4-trimethylpentane system can be used to determine the efficiency; for the other systems the error in determining the efficiency increases sharply as the value of the efficiency increases in the interval 0-80 plates. If the method of differential reading on a precision refractometer

* It should be mentioned that the components of the systems listed in Table 1 are extremely stable to boiling. As a result of this it is possible to operate with the same solution daily for a month, making occasional correction for amount and composition.

TABLE 3

Concentration Intervals, Number of Plates Corresponding to Them, and Error in Number of Plates, Fixed by the Errors in Determining the Concentrations from the Refractive Indices [the errors in reading the refractive indices were taken equal to $\pm 1 \times 10^{-4}$ and $\pm 1 \times 10^{-5} n_D^{20}$ (underlined figures)]

Concentration intervals (in mole %)	Benzene–carbon tetrachloride		Methylcyclohexane-2,2,4-trimethylpentane		Methylcyclohexane-n-heptane		1,2-Dichloroethane-benzene		n-Heptane-benzene	
	No. of plates	error in number of plates	No. of plates	error in number of plates	No. of plates	error in number of plates	No. of plates	error in number of plates	No. of plates	error in number of plates
8—60	22	0.2, 0.1	50	0.6, 0.3	41	0.5, 0.2	30	0.2, 0.1	5	0.04, 0.01
8—70	27	0.2	61	0.5	48	0.2	37	0.1	6	0.01
8—80	40	0.4	77	0.7	56	0.3	44	0.2	7	0.01
8—85	50	0.6	87	1.0	61	0.4	50	0.2	8	0.02
8—90	68	1.3	103	1.5	68	0.5	56	0.2	10	0.04
8—92	82	2.1	112	2.0	72	0.7	60	0.3	11	0.04
8—94	104	4.0	123	2.7	77	0.9	64	0.4	13	0.06
8—95	121	5	130	3	80	1.0	67	0.5	15	0.08
8—96	147	8	139	4	83	1.3	70	0.6	16	0.11
8—97	190	14	151	5	88	1.7	74	0.7	19	0.16
8—98	275	30	167	8	94	2.7	79	1.1	23	0.3
8—99	525	133	196	16	105	5	87	1.8	32	0.9
8—99.9			293	17	140	5	111	1.5	66	9

($\pm 1 \times 10^{-5} n_D$) is used to determine the concentrations, then in the interval of 80-200 plates it is possible to determine the efficiency using two systems: methylcyclohexane–2 2, 4-trimethylpentane and benzene–carbon tetrachloride.* Above 200 plates the system benzene–carbon tetrachloride must be used to determine the efficiency In Table 4 we have given the highest efficiencies that can be determined, using the precision refractometer, with the aid of the discussed systems and the corresponding errors in the efficiencies, expressed in per cent of the determined number of plates.

As a result, when compared with the other systems, the systems methylcyclohexane–2, 2, 4-trimethylpentane and benzene–carbon tetrachloride prove to be more universal in the sense that using them makes it possible to determine both small and very high efficiencies. The amount of time and labor consumed in purifying the components is nearly the same for all of the discussed systems. Methylcyclohexane, 2, 2, 4-trimethylpentane and n-heptane are difficultly available compounds. For this reason we usually used the system benzene–carbon tetrachloride to determine the efficiencies; in this connection we used an Abbe refractometer to determine the concentrations when the composition of the liquid in the condenser was below 85 mole % CCl_4, and the technique of differential recording on the drum of a Pulfrich refractometer when the concentration was above this value.

Up to now the system methylcyclohexane–n-heptane is used in those cases where it is desired to obtain the most accurate and reliable values for the efficiency, i.e., up to now preference has been given to this system over all other systems proposed for determining the efficiency. This is due to the simplicity and accuracy with which the number of plates using the system methylcyclohexane–n-heptane is calculated. The reason for this is that this system, according to the experimental data of Calingaert and Beatty, behaves almost like an ideal system [10]. For an ideal system the slope of the line $\alpha = f(x)$, where α is the relative volatility and x is the concentration of the low-boiling component in the liquid, is so small that the number of plates can be accurately calculated from the average value of α even for very large concentration intervals, for example 0.01-99.99 mole %. As soon as accurate data for constructing the diagrams of number of plates vs. concentration appeared for the

*The method of differential reading is more complicated than using the Abbe refractometer to determine the concentrations for the reason that it requires larger volumes of the liquid samples (1.5-3 ml), necessitates maintaining a more constant temperature (± 0.02°) for the water entering the sleeve of the refractometer, and consumes more time (to establish the desired temperature the investigated liquid must be kept in the cuvette for at least 4 minutes).

TABLE 4

Highest Efficiencies that Can Be Determined Using the Precision Refractometer ($\pm 1 \times 10^{-5} n_D^{20}$)

System	Number of plates	Error* in determining the number of plates (in %)
n-Heptane–benzene	66	1.4
1, 2-Dichloroethane–benzene	110	1.5
Methylcyclohexane–n-heptane	100	1.0
	140	4.0
Methylcyclohexane–2, 2, 4-trimethylpentane	200	1.1
	290	6.0
Benzene–carbon tetrachloride	200	0.8
	300	1.3
	500**	2.5

*The total errors (still pot, condenser) are indicated here, in which connection an Abbe refractometer was used to determine the composition of the liquid in the still pot (8 mole %), while the precision refractometer was used to determine the composition of the reflux from the condenser.

**That it is possible to determine such a large number of plates, even if indirectly, was shown by us experimentally [2].

discussed systems, this advantage of the system methylcyclohexane–n-heptane disappeared. In other respects this system, as can be seen from Tables 1, 3 and 4, is in no way better than the other systems and is even inferior to some of them.

The results of comparing the efficiencies of the same column, determined using different systems, are described in a previous communication [11]. It proved that the relationships between the efficiencies, determined using any two binary systems, at a constant reflux intensity, are independent of both the reflux intensity and the type of packing, and as follows from all of our studies, the efficiency is also independent of the solution concentration. The efficiencies, determined using the systems benzene–carbon tetrachloride, methylcyclohexane–2,-

TABLE 5

$$\text{Coefficient } \beta = \frac{\text{efficiency based on given system}}{\text{efficiency based on system benzene–carbon tetrachloride}}$$

The Efficiencies are Determined at Constant Reflux Intensities (in ml/minute per sq cm of column cross-section)

System	β
Benzene–carbon tetrachloride	1.00
Methylcyclohexane–2, 2, 4-trimethylpentane	0.98
Methylcyclohexane–n-heptane	1.07
1,2-Dichloroethane–benzene	1.18
n-Heptane–benzene	0.76

2, 4-trimethylpentane, methanol–acetone and acetic acid–ethyl acetate, are all the same; the efficiencies, using the systems methylcyclohexane–n-heptane and dichloroethane–benzene, are higher, while those obtained using the system n-heptane–benzene are lower, than the efficiencies obtained using the first group of systems.

Considering that the systems methylcyclohexane–2, 2, 4-trimethylpentane and benzene–carbon tetrachloride can be used to determine both small and very high efficiencies, that the efficiencies determined with their aid are the same and coincide with the efficiencies of some other systems, and finally that using these systems we obtain values for the efficiency that lie between those obtained using the systems dichloroethane–benzene, methylcyclohexane–n-heptane and n-heptane–benzene, we propose selecting the systems methylcyclohexane–2, 2, 4-trimethylpentane and benzene–carbon tetrachloride as standards.

Up to 80 plates, any of the systems listed in Table 1 (except n-heptane–benzene) can be used to determine the efficiency, but after this the obtained efficiency must be converted to the standard, which is achieved by dividing the obtained efficiency by the coefficient β.

The values of the β coefficients for the systems discussed in the present paper are given in Table 5.

SUMMARY

A comparison was made of the suitability of the following systems for determining the efficiencies of rectification columns: benzene–carbon tetrachloride, methylcyclohexane–2, 2, 4-trimethylpentane, methylcyclohexane–n-heptane, 1, 2-dichloroethane–benzene, and n-heptane–benzene.

It was shown that in general the system n-heptane–benzene is not suitable for the indicated purpose; up to approximately 80 plates, the number of plates can be determined with nearly the same degree of accuracy using any of the other 4 systems; above 80 plates, using the Abbe refractometer ($\pm 1 \times 10^{-4} n_D$), only the system methylcyclohexane–2, 2, 4-trimethylpentane can be used to determine the efficiency; if the method of differential reading on a precision refractometer ($\pm 1 \times 10^{-5} n_D$) is used to determine the concentrations, then in the interval from 80 to 200 plates both the methylcyclohexane–2, 2, 4-trimethylpentane and the benzene–carbon tetrachloride systems can be used to determine the efficiency; above 200 plates the efficiency should be determined using the benzene–carbon tetrachloride system.

It was proposed to select the systems methylcyclohexane–2, 2, 4-trimethylpentane and benzene–carbon tetrachloride as standards.

Up to 80 plates the efficiency can be determined using any of the above-enumerated systems, and then it must be converted to the standard. A table of coefficients for making such conversion is given.

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STUDY OF SOLUBILITY IN SYSTEM $NaF-NaCl-Na_2CO_3-H_2O$ AT 25 AND 50°

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Solutions containing sodium fluoride, sodium chloride and sodium carbonate will be obtained when sodium fluoride is prepared by the decomposition of sodium fluosilicate with sodium carbonate. Since a cyclic process is rational for the preparation of sodium fluoride, then to design such it is necessary to know the solubility in the quaternary system $NaF-NaCl-Na_2CO_3-H_2O$. Preliminary calculations revealed that it is necessary to know, at the least, the equilibria existing in this system at 25 and 50°.

The quaternary system, composing the recycled mother liquor, contains three ternary systems: $NaF-Na_2CO_3-H_2O$, $NaF-NaCl-H_2O$, and $NaCl-Na_2CO_3-H_2O$.

Only for the last two systems is there copious data in the literature [1]. The results obtained in investigating the second system at 25° are contradictory. Thus, for example, Foote [2] found 0.31% sodium fluoride and 26.12% sodium chloride at the eutectic point, while Campbell [3] found 1.06 and 26.6%, respectively. The first system has not been studied.

EXPERIMENTAL

The isothermal method was used to study the solubility. The salt mixtures were placed in plexiglas flasks, which were stoppered with plexiglas stoppers. Then, to ensure a tight seal, rubber caps were drawn over the stoppers. This was followed by placing the flasks in a thermostat, where a mercury-toluene thermoregulator automatically kept the water temperature constant with an accuracy of ± 0.1°.

Sodium fluoride was prepared by mixing solutions of ammonium fluoride and sodium carbonate, followed by drying the precipitate at 100° and ignition at around 700°. Ammonium fluoride was obtained by saturating c.p. hydrofluoric acid with gaseous ammonia. The sodium fluoride analyzed 99.96% pure. Sodium carbonate decahydrate was prepared by the crystallization of c.p. sodium carbonate from water solution. The sodium chloride used was c.p. grade.

Since equilibrium is reached very slowly when sodium fluoride is dissolved, the prepared mixtures were kept in the flasks for 1.5 to 2 months at room temperature with periodic mixing. After this they were placed in the thermostat for a day at 25°. The time required to reach equilibrium at 50°, without prior standing, was 5 days. For systems not containing solid sodium fluoride, the calculated amount of saturated sodium fluoride solution was added to the mixture. For the eutectic points, equilibrium was also reached from the supersaturation side. In this case we used 3.7% sodium fluoride solution, i.e., supersaturated with respect to the composition of the solution at the eutectic point, and crystalline sodium chloride and sodium carbonate decahydrate (or the anhydrous form for the mixtures at 50°) in making up the mixtures. Supersaturation with the last two components was rapidly reached by keeping the mixtures at an elevated temperature. The amount of salts was taken such that the solid phase did not disappear on heating, since otherwise supersaturated solutions are obtained. The agreement of the results, obtained using the two different ways of reaching equilibrium, served as evidence that the system was truly in equilibrium.

A stainless steel siphon was used to take the samples through a dense cotton plug. A heating mantle was drawn over the siphon when operating at 50°. The density of some of the solutions was determined using a pycnometer with ground-glass connections. The saturated solutions and wet residues were analyzed as follows.

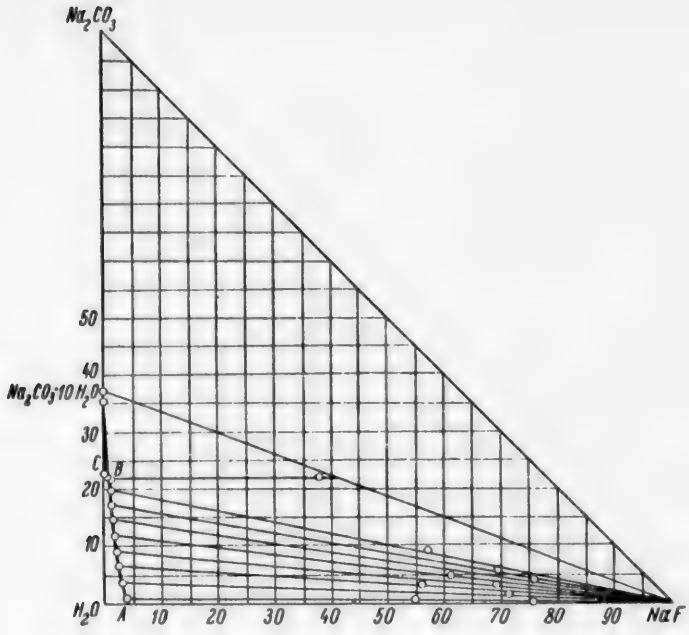

Fig. 1. Isotherm of system $NaF-Na_2CO_3-H_2O$ at 25°.

Chloride ion was determined by Volhard titration [4] with standard silver nitrate solution. The amount of carbonate was determined by neutralization with standard sulfuric acid solution. After removal of the CO_2 by boiling, the excess sulfuric acid was titrated with standard caustic solution using phenolphthalein. Fluoride in the solutions was determined as lead chloride fluoride by the Kapfenberger method [5]. The method was checked on synthetic mixtures and gave a relative error of 1-3% when the sodium fluoride concentration was above 0.1%. To verify the validity of the analyses, we took a number of solutions and determined the amount of sodium by conversion of the chlorides, fluorides and carbonates to sulfates. The amount of fluoride in the wet residues was not determined directly, but instead it was calculated by difference after determining the amount of sodium as sulfate, and also the amount of chloride and carbonate by the indicated methods.

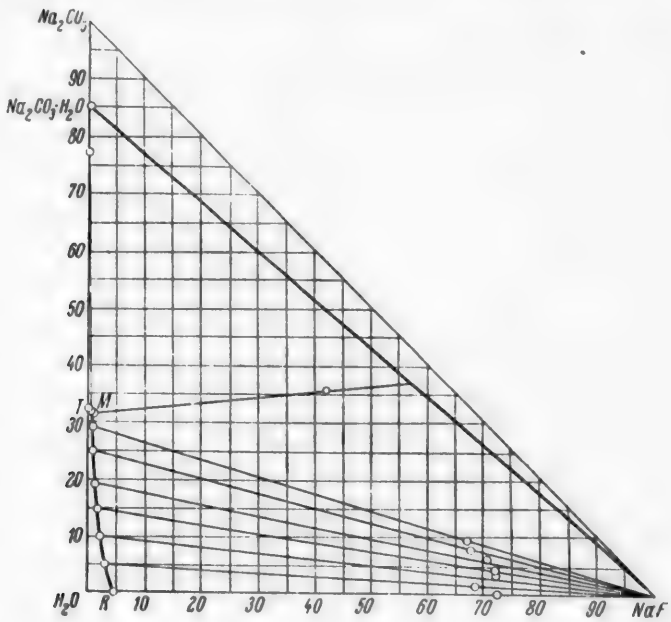

Fig. 2. Isotherm of system $NaF-Na_2CO_3-H_2O$ at 50°.

TABLE 1

Solubility in System $NaF-Na_2CO_3-H_2O$ *

Points	Composition of saturated solution (in wt. %)				Composition of residue (in wt. %)		d	Solid phases
	NaF	Na_2CO_3	total salts	H_2O	NaF	Na_2CO_3		
				Temperature 25° d_4^{25}				
A	3.77	0	3.77	96.23	75.61	0		
	3.45	0.86	4.31	95.69	54.40	0.65		
	2.78	3.52	6.30	93.70	70.79	1.39		
	2.17	6.55	8.72	91.28	55.73	3.26		
	1.92	9.09	11.01	88.99	69.06	3.09		NaF
	1.35	11.87	13.22	86.78	60.95	4.78	1.1406	
	1.38	14.91	16.29	83.71	75.54	4.04	1.1736	
	1.33	17.39	18.72	81.28	69.35	5.61		
	1.04	19.97	21.01	78.99	56.70	9.27		
B	1.04	21.83	22.87	77.13	38.71	20.17	1.2483	$NaF + Na_2CO_3 \cdot 10H_2O$
	0.52	22.22	22.74	77.26	0.36	35.40		
	0.25	22.43	22.68	77.32	0.02	35.33		$Na_2CO_3 \cdot 10H_2O$
C	0	22.51	22.51	77.49	0	35.34		
				Temperature 50°, d_4^{50}				
R	3.97	0	3.97	96.03	72.51	0	1.0307	
	2.76	4.95	7.71	92.29	68.82	1.52	1.0691	
	2.05	9.71	11.76	88.24	72.20	3.25	1.1098	
	1.48	14.61	16.09	83.91	72.30	4.30	1.1606	NaF
	1.02	19.23	20.25	79.75	70.57	6.32	—	
	0.79	24.63	25.42	74.58	67.60	8.17	1.2619	
	0.80	29.34	30.14	69.86	67.30	10.65	1.3207	
M	0.62	31.42	32.04	67.96	42.07	35.18	1.3417	$NaF + Na_2CO_3 \cdot H_2O$
	0.13	32.05	32.18	67.82	Traces	77.58	—	
T	0	32.15	32.15	67.85	0	83.46	—	$Na_2CO_3 \cdot H_2O$

*Laboratory technician M. A. Groznykh performed the analyses.

TABLE 2

Solubility in System $NaF-NaCl-H_2O$ at 50°

Points	Composition of saturated solution (in wt. %)				Composition of residue (in wt. %)		d_4^{50}	Solid phases
	NaF	NaCl	total salts	H_2O	NaF	NaCl		
R	3.97	0	3.97	96.03	72.51	0	—	
	3.07	2.59	5.66	94.34	73.24	0.21	—	
	1.71	8.84	10.55	89.45	79.54	1.30	—	NaF
	0.84	16.65	17.49	82.51	82.57	2.91	1.1142	
	0.62	20.33	20.95	79.05	79.40	4.12	1.1426	
	0.53	26.04	26.57	73.43	77.60	5.35	1.8410	
L	0.39	26.54	26.93	73.07	20.10	70.34	1.1888	NaF+NaCl
	0.27	26.55	26.82	79.18	Traces	93.1	—	
	0.18	26.68	26.86	73.14	»	94.8	—	NaCl
F	0	26.72	26.72	73.28	0	94.85	1.1908	

TABLE 3

Solubility in System $NaF-NaCl-Na_2CO_3-H_2O$

Points	Composition of saturated solution (in wt. %)					Composition of dry salts (in wt. %)			d	Solid phases
	NaF	NaCl	Na_2CO_3	total salts	H_2O	NaF	NaCl	Na_2CO_3		
					Temperature 25°				d_4^{25}	
G	0.40	26.37	0	26.77	73.23	1.49	98.51	0	1.1993	
	0.38	23.79	4.17	28.33	71.67	1.34	83.94	14.72	1.2254	
	0.30	21.41	8.17	29.88	70.12	1.00	71.65	27.35	1.2507	NaF + NaCl
	0.24	18.50	11.81	30.55	69.45	0.79	60.55	38.66	1.2745	
	0.23	16.14	15.68	32.05	67.95	0.72	50.36	48.92	1.2973	
H	0.23	15.17	17.30	32.70	67.30	0.70	46.39	52.91	1.3097	$NaF + NaCl + Na_2CO_3 \cdot 7H_2O$
	0.26	12.80	18.43	31.49	68.51	0.82	40.65	58.53	1.3044	$NaF + Na_2CO_3 \cdot 7H_2O$
Q	0.27	11.71	19.04	31.02	68.98	0.87	37.75	61.38	1.3013	$NaF + Na_2CO_3 \cdot 7H_2O + Na_2CO_3 \cdot 10H_2O$
	0.33	10.90	19.21	30.44	69.56	1.08	35.81	63.11	1.3011	
	0.40	10.53	19.15	30.08	69.92	1.33	35.01	63.66	1.3011	$NaF + Na_2CO_3 \cdot 10H_2O$
	0.39	10.41	18.62	29.42	70.58	1.32	35.39	63.29	—	
	0.64	5.47	19.18	25.29	74.71	2.53	21.63	75.84	—	
E	0	15.30	17.49	32.79	67.21	0	46.66	53.34	—	$NaCl + Na_2CO_3 \cdot 7H_2O$
	0.07	15.32	17.40	32.79	67.21	0.22	46.72	53.06	—	
					Temperature 50°				d_4^{50}	
	0.27	24.78	2.99	28.02	71.98	0.96	88.36	10.68	1.2093	
	0.23	22.31	6.78	29.28	70.72	0.78	76.19	23.03	1.2336	NaF + NaCl
	0.23	19.67	11.55	31.45	68.55	0.73	62.55	36.72	1.2673	
N	0.23	18.30	13.47	32.00	68.00	0.72	57.18	42.10	1.2785	$NaCl + NaF + Na_2CO_3 \cdot H_2O$
	0.32	8.85	22.67	31.84	68.16	1.00	27.80	71.20	1.3043	
	0.33	6.04	24.98	31.35	68.65	1.06	19.26	79.68	1.3115	$NaF + Na_2CO_3 \cdot H_2O$
	0.33	2.42	28.60	31.35	68.65	1.06	7.72	91.23	1.3326	
P	0	18.37	13.63	32.0	68.00	0	57.41	42.59	1.2808	$NaCl + Na_2CO_3 \cdot H_2O$

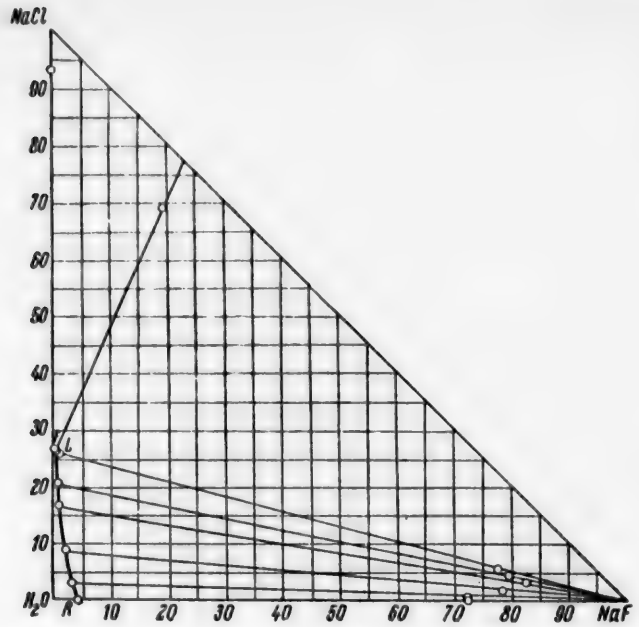

Fig. 3. Isotherm of system NaF—NaCl—H_2O at 50°.

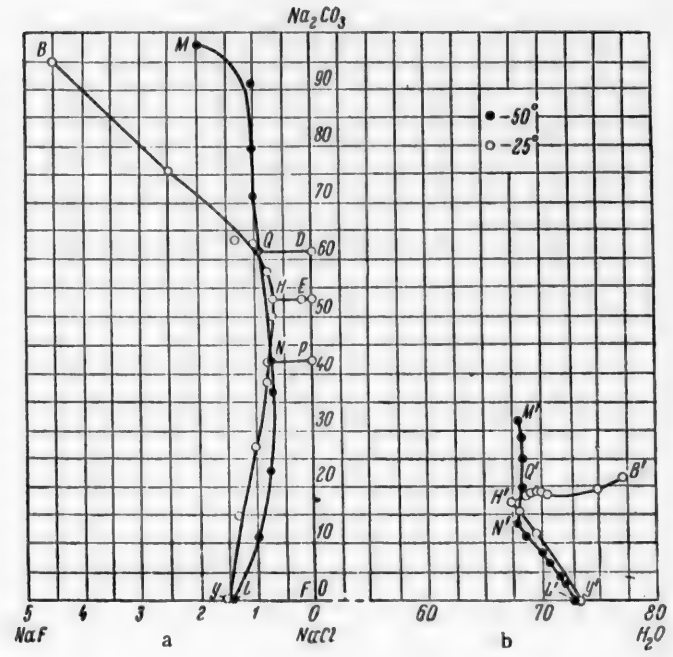

Fig. 4. Isotherms of system NaF—NaCl—Na_2CO_3—H_2O at 50° and 25°.

The composition of the solid phases was determined using the Schreinemakers method [6], and also from the refractive indices of the crystals, determined using a polarization microscope. The latter values prove to be especially important for these cases where the deca- and heptahydrates of sodium carbonate crystallize jointly.

DISCUSSION OF RESULTS

The results of studying the equilibria existing in the ternary system sodium fluoride—sodium carbonate—water at 25 and 50° are given in Table 1. The isotherms constructed from these data (Figs. 1 and 2) each have

two branches corresponding to the solid phases: $Na_2CO_3 \cdot 10H_2O$ and NaF at 25°, and $Na_2CO_3 \cdot H_2O$ and NaF at 50°, found in equilibrium with saturated solutions. As the temperature is increased, the amount of sodium fluoride at the eutectic point decreases from 1.04% at 25° to 0.62% at 50°.

The data for the system sodium chloride–sodium fluoride–water at 50° (Fig. 3) are given in Table 2.

When the eutectic point of this system at 25° was checked, it proved that the composition of the solution was close to that reported by Foote (0.40% NaF and 26.37% NaCl) and differed but slightly from the eutectic solution at 50°.

The quaternary system was investigated at 25° and 50°.

The results are given in Table 3 (Fig. 4). From the obtained data it can be seen that neither double salts nor solid solutions are formed in the quaternary system, the same as is true of the ternary systems that compose it. The addition of small amounts of sodium chloride to solutions saturated in sodium fluoride and sodium carbonate causes the sodium fluoride to salt out, and its solubility changes sharply.

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AMOUNT OF "INACTIVE" SULFUR IN SULFONIC ACID ION-EXCHANGE RESINS

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Together with ionogenic groups, ionites frequently also contain smaller amounts of other functional groups, devoid of ionogenic properties. Because of the great difficulties associated with determining the latter in insoluble crosslinked polymers, it becomes necessary for the most part to only conjecture as to their character. Thus, for example, the reducing properties of phenol-formaldehyde ionites [1] are explained by the presence of easily oxidized groups, in all probability being of the aldehydic, quinoidal, etc., type.

The authors of the present paper have shown that many of the sulfonic acid ionites studied by them, prepared from various organic compounds, contain, besides "active" sulfur, present as the sulfonic group and easily determined by titration [2], also smaller amounts of "inactive" sulfur (Table 1).

The presence of the latter can be shown by comparing the results obtained in determining the sulfur by elemental analysis (S) and by titration (S_a).

Up to now the problem of the amount of inactive sulfur in sulfonic acid resins has failed to attract the attention of investigators, in which connection it is possible to encounter vague statements in the literature regarding the relationship between the exchange capacity of ionites and their total sulfur content [3].

Inactive sulfur can be present in ionites in the form of various compounds or groups, already contained in the starting materials, or it can be of secondary origin, i.e., it can be formed during sulfonation or in the subsequent operations of preparing the ionites. For example, sulfo carbons usually contain some sulfide and sulfate sulfur (as FeS_2, $FeSO_4$, $CuSO_4$, etc.); ionites obtained by the sulfonation of rubber [4] contain vulcanization sulfur, etc. In studying the process for the formation of sulfo ionites, much more attention should be given to the inactive sulfur of secondary origin.

Based on experimental data [5], we had previously expressed a theory regarding the character of the sulfur-containing functional nonionogenic groups found in insoluble phenol-formaldehyde sulfo resins and their role in the formation of such resins [6]. It is quite probable that the inactive sulfur in sulfo phenol ionites is present as sulfo ester and sulfonic groups, taking part in the processes of "crosslinking" soluble sulfonic acids. As a result, the question of the amount of inactive sulfur in ionites possesses interest when studying the mechanism for the formation of insoluble sulfo polymers. In this connection the choice of methods for determining the total amount of sulfur in sulfo ionites assumes importance, and from this the amount of sulfur contained in the nonionogenic functional groups, based on the difference $S-S_a$. Such determinations, naturally, should precede investigating the chemical nature of the inactive sulfur present in sulfo ionites of various origins.

We scrutinized a variety of analysis methods. Those reported in the literature were modified in one respect or another.

It was established that some of the methods, where the substance is subjected to oxidative decomposition in either acid or alkaline medium and the sulfur is then determined as barium sulfate, prove to be unsuitable for the analysis of sulfo ionites.

TABLE 1

Comparison of Results of Determining Sulfur in Sulfo Ionites by the Method of Fusion with KNO_3 and KOH and Subsequent Titration in the Presence of NaCl

Ionite	Amount of sulfur in ionite		$S - S_a$ (in %)	$\frac{S - S_a}{S} \cdot 100$ (in %)
	determined as S by fusion with KNO_3 [9] (in %)	determined as S_a by titration (in %) [2]		
Sulfo-hydrocarbon ionites:				
SDV-3	12.50	12.03	0.47	3.76
KU-2	16.17	15.52	0.65	4.02
SBS-3	12.84	11.18	1.66	12.9
SSF	14.91	12.90	2.01	13.5
Sulfo-phenol ionites:				
Duolite C-3	11.10	10.71	0.39	3.51
Amberlite IR-100	6.32	6.04	0.28	4.42
KU-1	8.62	7.25	1.37	15.9
PFSK	9.48	7.81	1.67	17.6
SNF	11.07	9.25	1.82	16.5
SN	13.84	11.62	2.22	16.1

The oxidation of ionites using a mixture of nitric acid and bromine [7], or nitric acid and hydrogen peroxide, or an alkaline potassium permanganate solution at the boil (Messinger method [8]), gave low results. Evidently, incomplete oxidation is obtained when the indicated wet methods and conditions are used to oxidize sulfo resins.

Entirely, satisfactory results were obtained with the following methods: fusion of the resin with potassium permanganate and sodium carbonate, followed by boiling the melt with hydrochioric acid to dissolve the manganese dioxide; and fusion with potassium nitrate and potassium hydroxide (or sodium hydroxide), followed by dissolving the melt in water (Liebig method [9]), and precipitating the sulfur as barium sulfate. The first method requires quite a long time to dissolve the MnO_2, and for this reason preference was given to the more rapid second method.

The micromethods enumerated below, based on the catalytic reduction or oxidation of organic substances, were used with success to determine the sulfur in sulfo ionites.

When the method of Korshun and Gel'man [10] was used, the hydrogen sulfide formed by decomposition of the substance in a stream of hydrogen was absorbed in zinc sulfate solution, and the obtained sulfide was determined by iodometric titration.

When the gravimetric method of Korshun and Sheveleva [11] was used, the sulfur oxides formed by burning the substance in a stream of oxygen were absorbed on silvered pumice [12]. The method permits the simultaneous determination of carbon, hydrogen and sulfur.

When the volumetric method worked out basically by Pregl [13] was used, the sulfur oxides formed by burning the substance in a stream of oxygen were absorbed in hydrogen peroxide solution, followed by titration of the formed sulfuric acid. The apparatus used in analyzing the ionites was analogous to that recommended for the determination of halides [14].

A rapid method, in which the weighed sample of resin was burned in a flask filled with oxygen, was also used to determine sulfur in sulfonic acid ionites. The oxides were absorbed in dilute hydrogen peroxide solution, previously poured into the same flask. The apparatus that we used here had been recommended earlier for the rapid determination of halides [15].

The results of determining sulfur using different methods, giving satisfactory results when applied to sulfonic acid ionites, are compared in Tables 1-3.

TABLE 2

Comparison of Results of Determining Sulfur in Sulfo Ionites by the Methods of Fusion with KNO_3 and KOH and of Reductive Decomposition

Ionite	Amount of sulfur in ionites		$S - S'$ (in %)	$\frac{S-S'}{S} \cdot 100$ (in %)
	determined as S by fusion with KNO_3 and KOH [9] (in %)	determined as S' by dry combustion in stream of H_2 (%) [10]		
Sulfo-hydrocarbon ionites:				
KU-2	16.17	15.55	0.62	3.89
SBS-R	8.91	8.55	0.36	4.04
Sulfo-phenol ionites:				
KU-1	8.62	8.37	0.25	2.90
Amberlite IR-100	6.32	6.11	0.21	3.32
Wofatit P	4.70	4.51	0.19	4.04

The values of $\frac{S-S_a}{S}$ (Table 1) for ionites SDV-3, KU-2, Duolite C-3 and Amberlite IR-100 range from 3.5 to 4.4%, whereas for ionites SBS-3, SSF, KU-1, SNF, SN and PFSK the values range considerably higher (12.9-17.6%).

The analysis values given in Table 2 show that the method of fusing the substance with KNO_3 and KOH, and determining the sulfur as $BaSO_4$, constantly gives higher results than the micromethod of reductive decomposition, in which connection the values of $\frac{S-S'}{S}$ for different ionites range from 2.9 to 4.0%, i.e., very close to the values of $\frac{S-S_a}{S}$ for some of the ionites included in Table 1. As a result, there is reason to believe that of the two methods for determining sulfur the reductive micromethod is characterized by the greater accuracy, and for ionites SDV-3, KU-2, Duolite C-3 and Amberlite IR-100 the differences between the values of S and S_a are actually small, i.e., the indicated ionites are practically devoid of inactive sulfur.

The validity of the last assumption, and consequently the accuracy of the values obtained by the method of dry combustion in a stream of hydrogen, is confirmed by the data given in Table 3, from which it can be seen that the parallel determinations of sulfur in SNF ionites using four microanalytical methods, including the destructive reduction method, give extremely close results. Earlier [16], on the examples of ionites KU-1 and KU-2, we had shown that the method of determining sulfur in ionites by fusion with KNO_3 and KOH gives somewhat high results, which is explained as due to joint precipitation when the sulfur is determined as $BaSO_4$.

The data, given in the present communication, confirm the results of these experiments [16]. For cationites SBS-3, SSF, KU-1, SNF, SN and PFSK the values of $\frac{S-S_a}{S}$ are substantial (12.9-17.6) and cannot be explained as due only to joint precipitation, but instead indicate that inactive sulfur is present in the ionites.

Despite the simplicity of determining sulfur in ionites by fusion of the substance with potassium nitrate and potassium hydroxide, and the adequate reproducibility of the analysis results, still preference should be given to the above-indicated micromethods in view of their greater accuracy and the much smaller amount of time required to run the analyses (usually 40 to 50 minutes instead of 5 hours). When compared with the micromethods of burning the substance in either a stream of hydrogen or oxygen, the method of combustion in a flask filled with oxygen possesses undoubted advantage; to run the analysis requires very simple apparatus, and the length of each determination does not exceed 15-20 minutes.

TABLE 3

Comparison of Results of Determining Sulfur in Sulfo Ionites SNF by Microanalytical Methods of Destructive Reduction and Oxidation•

Sample No.	Amount of sulfur in ionites (in %), determined using the methods				Remarks
	dry combustion in a stream of hydrogen [10]	dry combustion in a stream of oxygen in a quartz tube		combustion in an atmosphere of oxygen in a flask	
		gravimetric determination [11, 12]	volumetric determination [13, 14]		
1	7.35	7.42	7.39	7.41	
2	9.87	–	9.97	–	
3	10.03	10.21	10.09	10.06	
4	10.07	10.22	9.81	10.06	
β-Naphthalene-sulfonic acid $C_{10}H_8O_3S \cdot 3H_2O$	12.28	12.11	12.07	–	Theoretical amount of sulfur 12.23%

•The determinations were run in parallel (using different methods). In the table we have given the average values, calculated for the air-dried ionite samples.

EXPERIMENTAL•

The H-form of the air-dried ion-exchange resin was ground in an agate mortar to a fine powder, known amounts of which were then taken sulfur determination. The amount of moisture in the samples was determined at the same time by drying 1.5-2 g of the resin in a drying oven at 105-110° to constant weight. The amount of active sulfur was determined by titrating the ionites in the presence of sodium chloride solution using methyl orange as the indicator [2].

Determination of sulfur in ionites by fusion with potassium nitrate and potassium hydroxide [9]. A mixture of 0.8 g of KNO_3 and 4 g of KOH was fused in a silver crucible placed in a retort furnace. After cooling, the crucible was weighed, and then about 0.2 g of the ionite was added. Further heating caused the resin to gradually decolorize. After cooling the crucible, the homogeneous melt was dissolved in water and the solution was transferred to a flask. The subsequent operations were carried out in customary manner, i.e., the solution was made acid with hydrochloric acid, heated, the barium sulfate precipitated (using 15-20 ml of hot 0.5 N $BaCl_2$ solution), then filtered (the following day), washed with water, and ignited to constant weight.

The time required to run the analysis was about 5 hours (not including the time taken out to obtain complete precipitation of the $BaSO_4$).

Determination of sulfur by dry combustion in a hydrogen stream [10]. A 3-6 mg sample of the ionite was burned in a quartz tube containing platinum catalyst for 20 min in a stream of hydrogen, passed through the tube at a rate of 20-25 ml/min. Then the formed hydrogen sulfide was displaced by hydrogen, passed through the tube at a rate of 50-80 ml/min for 5-10 min. The hydrogen sulfide was absorbed by a mixture of equal parts of 10% $ZnSO_4$ and 10% CH_3COONa, acidified with several drops of concd. acetic acid. The obtained sulfide was determined iodometrically. The total time of the analysis was 50-60 min.

Gravimetric determination of sulfur by dry combustion in an oxygen stream [11, 12]. A 3-6 mg sample of the ionite was burned in a quartz tube containing platinum catalyst for 13-15 min in a stream of oxygen, passed

•V. S. Matrosova assisted in the experimental portion of this work.

through the tube at a rate of 35-50 ml/min. The formed sulfur trioxide was quantitatively absorbed on silvered pumice, heated to 650-700°. The amount of sulfur in the ionite was determined from the weight increase of the absorption apparatus (due to the formation of Ag_2SO_4). The total time of the analysis was 40-45 min.

Volumetric determination of sulfur by dry combustion in an oxygen stream [13, 14]. A 3-6 mg sample of the ionite was burned in a quartz tube containing platinum catalyst in a stream of oxygen, passed through the tube at a rate of 20-25 ml/min. The quartz absorption apparatus was filled with either glass rings or helices moistened with neutral 5% hydrogen peroxide solution. A test tube with a sealed-in porous plate was connected to the absorption apparatus, and it was also filled with the same 5% hydrogen peroxide solution (to create a hydraulic seal). The final product of the sulfur oxidation, namely sulfuric acid, was titrated with 0.01 N NaOH solution using methyl red as the indicator. The total time of the analysis was 35-40 min.

Volumetric determination of sulfur by dry combustion in an oxygen atmosphere. The combustion was run in a pyrex Erlenmeyer flask, fitted with a ground-glass stopper and a side arm with a stopcock fitting. A 4-8 mg sample of the ionite was wrapped carefully in ashless filter paper, and the wad was placed on a platinum grid, fastened to one end of a platinum wire 60-70 mm long and with a diameter of 0.7-0.8 mm, sealed in the constricted end of a tube. After placing the absorbing liquid (3 drops of perhydrol in 10 ml of water), neutralized to alizarin red, in the flask, the flask was filled with oxygen, the filter paper was kindled, and the stopper was quickly inserted in the flask. The burning of the sample required 15-20 sec. The flask was shaken for 5-8 min until the fog over the liquid had disappeared, the pressure inside the flask was equalized with the external pressure, and the solution was boiled for 10 sec to remove CO_2.

The flask was cooled in water and the solution was titrated with 0.01 N NaOH solution using alizarin red as indicator. The time of the individual analyses did not exceed 15-20 min and could have been reduced even more.

SUMMARY

1. It was shown that in order to study the mechanism of formation and the structure of insoluble ion-exchange polymers it is important to have some knowledge regarding the character of the nonionogenic functional groups contained in them.

2. Based on the comparative determination of sulfur in sulfo ionites using different analysis techniques, it was shown that many ionites contain inactive sulfur that cannot be determined by titration, which sulfur is present in the nonionogenic groups (in all probability, sulfo ester and sulfonic groups).

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REDUCTION OF LANGBEINITE BY METHANE

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Langbeinite ($K_2SO_4 \cdot 2MgSO_4$) is a mineral that is found quite extensively in potassium salt deposits of the Carpathian region [1]. At the present time it is subjected only to enrichment (washing out of halite from the langbeinite rock) and under the name of "kalimag" is used as a poor potash fertilizer. At the same time this mineral, as well as the widely distributed kainite–langbeinite deposits, can serve as a source of potassium sulfate, an extremely valuable concentrated potash fertilizer.

The problem of containing K_2SO_4 from langbeinite reduces to its separation from $MgSO_4$. However, because of the ready solubility of both salts it is very difficult to accomplish this separation by wet methods. For this reason all of the methods proposed earlier for the wet processing of langbeinite proved to be both complicated and economically unfeasible [2-4]. Dry processing methods, based on the reduction of the $MgSO_4$ present in langbeinite to the water-insoluble magnesium oxide, with the K_2SO_4 remaining unchanged, offer much more promise. Here the separation of the K_2SO_4 from the MgO is no problem whatsoever.

Up to now only one method for the dry processing of langbeinite has been examined, in which charcoal was used as the reducing agent [5-7]. Here it was shown that it is possible to make the process go, but because of various technological and apparatus difficulties the process failed to find industrial application [8].

At the present time the use of natural gas (methane) for the reduction of langbeinite appears especially promising. Proceeding on this assumption, we decided to study the reduction of langbeinite with methane and determine if this new method of gaseous dry processing could be used to obtain K_2SO_4 from langbeinite.

First we investigated the methane reduction of the individual components present in langbeinite, namely $MgSO_4$ and K_2SO_4. It proved that reaction between $MgSO_4$ and methane begins at 710° and goes with considerable speed at 750°. The reaction products are MgO and various sulfur-containing compounds (SO_2, S, H_2S, CS_2), the proportions of which show profound variation depending on the reduction conditions. By making an exhaustive study of this reaction we were able to establish that the primary reduction product is SO_2, and that all of the other sulfur-containing products are obtained as the result of secondary reduction of the SO_2 by excess methane [9]. Consequently, the basic equation for the reduction of $MgSO_4$ with methane has the form

$$4MgSO_4 + CH_4 = 4MgO + 4SO_2 + CO_2 + 2H_2O. \quad (1)$$

The reduction of K_2SO_4 by methane does not begin before 800° and goes with the formation of mainly potassium polysulfides. The rate of reduction is quite slow even at 850° [10].

As a result, preliminary studies revealed that in principle it is possible to effect the selective reduction of langbeinite with methane, i.e., to effect the reduction of only $MgSO_4$ and leave the K_2SO_4 unchanged.

EXPERIMENTAL

The reduction of langbeinite with methane was studied using the apparatus shown in the figure. For the experiments we used the langbeinite concentrate "kalimag", with the composition (in %): 47.66 $MgSO_4$, 31.11 K_2SO_4, 2.58 $CaSO_4$, 2.04 NaCl, 4.86 insoluble residue, and 11.8 H_2O; the reducing agent used was natural (Dashavsk) gas* (methane). The weighed sample of dehydrated fine-grained (0.3-0.6 mm) langbeinite in a porcelain boat

*Composition of the natural gas (in %): CH_4 97.83, C_2H_6 0.44, C_3H_8 0.18, C_4H_{10} 0.05, C_5H_{12} and higher 0.11, and N_2 1.1.

TABLE 1

Effect of Temperature on Reduction of Langbeinite with Methane

Temperature	M*	Weight loss (in %)	Sulfur distribution (in %)						Extent of $MgSO_4$ reduction (in %)	Ratio $\frac{CO_2}{CO}$
			in solid residue		in gases					
			SO_4''	$S''+SO_3''$	SO_2	S	H_2S	CS_2		
760	1.5	13.9	75.0	Следы	1.2	3.1	15.6	5.1	37.6	8.3
800	1.5	29.0	36.9	3.3	2.0	20.9	27.0	9.9	89.5	8.3
800	1.0	27.3	—	0.7	2.2	—	24.6	—	—	—
840**	1.5	32.6	27.0	7.0	3.9	32.4	22.7	8.0	99.0	6.6
840	1.0	31.1	—	3.4	3.0	—	20.0	—	—	—
880***	1.5	29.1	45.8	0.4	4.2	19.4	28.1	2.1	80.6	4.5
880	1.0	27.0	—	0.9	3.6	—	24.7	—	—	—

*Here and subsequently M is the mole ratio $CH_4/MgSO_4$.

**Sintering.

***Residue molten. No S'' ion present.

was reduced in a stream of methane at a predetermined temperature in the quartz reactor tube of an electrically heated tube furnace.

The SO_2 and H_2S in the gaseous reaction products were determined iodometrically, the carbon-containing sulfur compounds were determined by combustion [11], while the CO_2 and CO were determined by conventional gas analysis methods. The solid residue was analyzed for loss in weight and amount of SO_4'' (gravimetrically) S'' and SO_3'' (iodometrically) ions. Elemental sulfur was found by difference.

By means of preliminary experiments it was established that the reduction of the $MgSO_4$ contained in langbeinite by methane begins to go quite rapidly at 750°. The effect of the temperature and time of reduction on this process can be seen from the data in Table 1. In this series of experiments the methane was admitted into the reactor at a rate of 10 ml/min, which sets the time of the experiments as M = 1.5 in 30, and M = 1.0 in 20 minutes. The extent of $MgSO_4$ reduction was determined from the amount of sulfur in the gaseous reaction products. The formation of S'' and SO_3'' ions in the solid residue was regarded as being due to the reduction of K_2SO_4 (and possibly $CaSO_4$).

From the obtained data it can be seen that the rate with which langbeinite is reduced by methane increases substantially as the temperature is raised to 840°, and then it shows noticeable decrease at higher temperatures (880°). This is apparently associated with a fusion of the residue at 880°.

In this connection only the $MgSO_4$ is reduced at temperatures up to 800°, but above this temperature the K_2SO_4 also begins to show substantial reduction. When the experiments run for different lengths of time at this temperature are compared, it is not difficult to see that the main reduction of the K_2SO_4 occurs toward the end of the process, when most of the $MgSO_4$ had already been reduced. And, judging from the weight loss and the yield of H_2S, the main portion of the $MgSO_4$ is actually reduced within 20 min. As a result, it is necessary to associate the reduction of K_2SO_4 as due more to the concentration of methane in the reaction zone than to the temperature of the process. At a low methane concentration (start of the process) the K_2SO_4 is hardly affected,* but at a higher concentration (end of the process) the reduction of the K_2SO_4 goes at a substantial rate.

Attention is attracted to the very low yield of sulfide–sulfite sulfur at 880° and the completely different character of its change with time (it decreases during the last 10 minutes). This is easily explained by the potassium sulfides (or polysulfides) reacting with the $MgSO_4$ in the melt [12]. As long as the residue remained solid, this secondary reaction hardly occurred.

*At the start of the process nearly all of the methane is consumed in the reduction of $MgSO_4$ and its residual concentration is small.

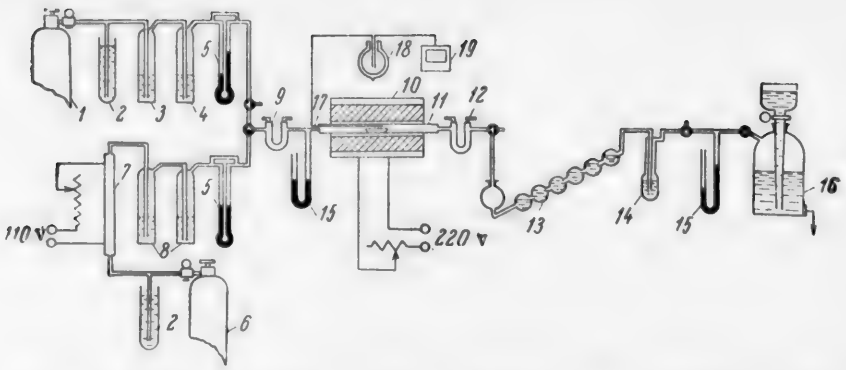

Diagram of apparatus. 1) Methane cylinder, 2) hydraulic seal, 3) scrubber containing concd. KOH, 4) scrubber containing concd. H_2SO_4, 5) flow meter, 6) nitrogen cylinder, 7) tube filled with copper turnings, 8) scrubber containing pyrogallol solution, 9) calcium chloride tube, 10) electrically heated tube furnace, 11) quartz tube ($\underline{l}$ = 400 mm, $\underline{d}$ = 20 mm), 12) filter for sulfur, 13) bulb absorber containing 0.1 N I_2 solution, 14) scrubber containing KI solution, 15) manometer, 16) evacuated gasholder, 17) TP-5 thermocouple, 18) Dewar flask, and 19) MP-1 galvanometer.

The physical properties of the product formed play an important part in determining the course of the process. Despite the fact that the eutectic temperature of the system K_2SO_4–langbeinite is equal to only 747° [13], still our product fails to melt up to 840°, and instead it sinters to a greater or less degree. This obviously is associated with the formation of infusible magnesium oxide, which up to a certain temperature can function as a thickener and impart a highly viscous consistency and porous structure to the grains of the residue (even when the residue proves to have the eutectic composition), not permitting it to melt. At $\underline{t}$ > 840° the magnesium oxide is no longer capable of keeping the product from melting. Reduction of the melt by the methane gas goes very poorly, for which reason the $MgSO_4$ present in langbeinite shows a quite low degree of reduction at 880°.

The composition of the gaseous reduction products varies considerably depending on the temperature of the process. The yields of the individual sulfur-containing gaseous products, based on the sulfur of the reduced $MgSO_4$ (calculated from the data of Table 1), are given in Table 2.

TABLE 2

Effect of Temperature on Composition of Gaseous Reaction Products

Temperature (in °C)	Extent of $MgSO_4$ reduction (%)	Sulfur distribution (in %)			
		SO_2	S	H_2S	CS_2
760	37.6	4.8	12.4	62.4	20.4
800	89.5	3.4	35.0	45.1	16.5
840	99.0	5.8	48.4	33.9	11.9
		Fusion			
880	80.6	7.8	36.1	52.2	3.9

As can be seen, raising the temperature up to the point where fusion of the residue occurs causes the yields of the individual products to change in a regular manner: the yield of free sulfur (and SO_2) increases substantially due to a decrease in S^{-2} (H_2S + CS_2). After fusion of the residue it is only for the SO_2 that the character of the change in the yield remains unchanged. This suggests that all of the SO_2 is formed at 880° even before the product melts.

TABLE 3

Distribution of Sulfur in the Reduction of Langbeinite and $MgSO_4$. t = 800°, v_{CH_4} = 10 ml/min, $CH_4/MgSO_4$ = 1.5

Salt	Extent of reduction (in %)	Distribution of S (in %)			
		SO_2	S	H_2S	CS_2
$K_2SO_4 \cdot 2MgSO_4$	89.5	3.4	35.0	45.1	16.5
$MgSO_4$	99.1	48.1	33.2	8.8	9.9

It is obvious that the mechanism for the reduction of the $MgSO_4$ present in langbeinite is the same as for pure $MgSO_4$. Consequently, the primary reaction here is also the formation of SO_2, proceeding in accordance with the equation

$$2[K_2SO_4 \cdot 2MgSO_4] + CH_4 = 2K_2SO_4 + 4MgO + 4SO_2 + CO_2 + 2H_2O. \quad (2)$$

All of the other sulfur-containing products are obtained as the result of secondary reduction of the SO_2 by excess methane.

However, when analogous experiments for langbeinite and $MgSO_4$ are compared, it can be seen that in the case of langbeinite the amount of H_2S in the products is increased substantially at the expense of a decrease in the amount of SO_2 (Table 3).

We believe that the course of the process can be explained in the following manner. The rate of the primary reaction (formation of SO_2) is considerably slower for langbeinite than for $MgSO_4$ (compare the extent of reduction). As a result of this, at the same methane feed rate, even in the initial stage of the process the intermediate ratio of SO_2/CH_4 in the reaction zone will be considerably smaller when langbeinite is reduced than when $MgSO_4$ is reduced. In this way, when langbeinite is reduced, more favorable conditions are created for progress of the secondary reduction of SO_2, and the main products become H_2S and S.

Increasing the temperature accelerates reaction (2), and this leads (maintaining the methane feed rate constant) to an increase in the intermediate ratio SO_2/CH_4. As a result of this the secondary reduction of SO_2 is less profound, i.e., the yield of S increases at the expense of a decrease in the yield of H_2S. The indicated rule is violated when the product melts, since here the rate of reaction (2) decreases sharply. This leads to a substantial decrease in the SO_2/CH_4 ratio in the reaction zone and to an increase in the amount of H_2S in the products.

As a result, the methane concentration in the reaction zone when langbeinite is reduced is an exceedingly important factor, determining both the composition of the gaseous products and the possibility of reducing the K_2SO_4 present in langbeinite. This caused us to make a separate study of the effect of the methane feed rate on the reduction process. This series of experiments were run at 800°, employing the ratio $M = CH_4/MgSO_4 = 0.5$. The results of the experiments are given in Table 4.

If the obtained data are compared with the data in Table 1, then it is easy to see that the extent of K_2SO_4 reduction actually decreases as the methane feed rate is decreased (i.e., as its concentration in the reaction zone is decreased). Also the composition of the gaseous products shifts toward those products that derive from a less profound reduction of the SO_2. Even at $\underline{v}$ = 2.5 ml/min the main gaseous product is elemental sulfur. It is obvious that at even slower methane feed rates the main product can be SO_2.• As a result, changing the methane concentration in the reaction zone makes it possible to run the process in such manner that either sulfur•• alone or pure sulfur dioxide is obtained as by-product.

•This was confirmed experimentally by taking a layer of langbeinite (10 cm long) and reducing it with a slow stream of methane. The gases escaping from the reactor were found to contain only one sulfur-containing product, namely SO_2.

••The other sulfur-containing gases (SO_2 and $H_2S + CS_2$), always obtained along with sulfur, are easily converted to elemental sulfur by passing the mixture of gases over a bauxite catalyst at low temperature [14].

TABLE 4

Effect of Methane Feed Rate on Reduction of Langbeinite

$\underline{v}$ (in ml/min)	Time (in min)	Weight loss (in %)	Sulfur distribution (in %)						Extent of $MgSO_4$ reduction (in %)
			in solid residue		in gas				
			SO_4''	$S'' + SO_3''$	SO_2	S	H_2S	CS_2	
10	10	16.5	58.7	0.07	2.3	22.2	10.0	6.8	38.2
5	20	24.6	39.3	0.20	9.8	43.8	4.1	2.8	90.7
2.5	40	27.0	33.0	1.02	11.5	49.4	2.9	2.2	99.0

The data given in Table 4 show that at low methane feedrates the ratio $M = CH_4/MgSO_4 = 0.5$ is sufficient to effect the complete reduction of the $MgSO_4$ present in langbeinite. Here the solid product contains very little potassium sulfide and hardly sinters. However, even with low methane feed rates a long residence of the salt in the reaction zone leads to noticeable reduction of the K_2SO_4.

From our experiments it follows that the time required to obtain practically complete reduction of the $MgSO_4$, and still not affect the K_2SO_4, is approximately 30 to 40 minutes.

It is interesting to mention that at $\underline{v}$ = 5 ml/min the extent to which the $MgSO_4$ in langbeinite is reduced in 20 min is considerably greater than at $\underline{v}$ = 10 ml/min in 30 min. As a result, an unexpected result is obtained: the rate of the process decreases as the relative concentration of methane in the reaction zone increases. But this is only a seeming contradiction. The truth of the matter is that our data refer only to the average rate of reduction. But it is obvious that the main influence (at constant temperature) on the reduction rate should be exerted by the properties of the surface layer of the already reduced langbeinite grains, since the rate with which methane diffuses into the grains is mainly dependent on these properties.

The higher the methane feed rate the faster the initial reduction rate. This leads to a noticeable fusion of the grains and their pronounced sintering, i.e., to the formation of a layer showing marked resistance to diffusion. Because of this the rate of the process decreases rapidly with time. The smaller the methane feed rate the slower the rate of the process at the start, the smaller the fusion of the surface layer (less sintering), and the smaller its resistance to diffusion. For this reason the decrease in the reduction rate with time goes much slower. As a result, a higher average rate for the process obtains at a smaller methane feed rate. A similar phenomenon was observed by Gorbanev when he used producer gas to reduce Na_2SO_4 [15], but he failed to give any explanation for it.

Our laboratory work indicates that it is entirely possible to subject langbeinite to reduction by methane and convert it to potassium sulfate, magnesium oxide and sulfur (or sulfur dioxide). The optimum conditions for the process are: temperature 800-820°, a low concentration of methane in the reaction zone, and a residence time of the salt in the reaction zone not exceeding 40 minutes. These conditions find complete technological acceptance. The close proximity of Dashavsk gas to the potassium deposits and the small amount needed for reduction (0.5 CH_4 per 1 $MgSO_4$) also make it possible to consider this process economically feasible.

SUMMARY

1. When the reduction of langbeinite ($K_2SO_4 \cdot 2MgSO_4$) by methane was investigated at different temperatures (700-900°) and different methane feed rates it was established that only $MgSO_4$ is reduced at 750-800°. A partial reduction of K_2SO_4 is possible only at $\underline{t} > 800°$ and with the simultaneous presence of a high methane concentration in the reaction zone. Based on the results of studying the reduction of $MgSO_4$ and K_2SO_4, the mechanism for the reduction of langbeinite with methane was discussed.

2. It was shown that it is possible to run the reduction of langbeinite at 760-840° without melting the product. Melting of the residue occurs at higher temperatures and it becomes very difficult to effect the complete reduction of the $MgSO_4$ present in langbeinite. It was also established that decreasing the methane

concentration in the reaction zone exerts a favorable influence on the average rate of the process, and also on the composition and structure of the reduction product.

3. The obtained experimental results indicate that it is possible to use a gas variation of the dry processing technique to convert langbeinite to potassium sulfate, magnesium oxide and sulfur.

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PROCESS OF PHOSPHATATION OF STEEL IN THE PRESENCE OF NITRATES OF TRIVALENT METALS AND NITRIC ACID (PART III)

I. I. Khain

We have shown previously [1, 2] that the process of phosphatation and the properties of the phosphate layer obtained are affected by the presence of nitrates of mono- and bivalent metals in the phosphatating solution, and that the importance of this effect depends on the degree to which a given salt is hydrolyzed.

It appears, therefore, of interest to investigate the effect of nitrates of trivalent metals which are strongly hydrolyzed in aqueous solutions.

We have also investigated the effect of free nitric acid on the phosphatation process.

EXPERIMENTAL

The samples, the phosphatating reagent, and the method of investigation remain the same as those described previously [1, 2].

The nitrates added to the phosphatating solutions were chemically pure aluminum, chromium and iron nitrates, and also nitric acid.

The results obtained are presented separately for nitrates of trivalent metals and nitric acid.

Effect of Aluminum, Chromium and Iron Nitrates

Aqueous solutions of aluminum, chromium, and iron nitrates are always acid due to hydrolysis, accompanied by liberation of free nitric acid. Addition of these nitrates to the solution of phosphates leads to a considerable increase of the acidity of the solution (Fig. 1).

It must be noted that in the solution of primary phosphates of iron and manganese there is ordinarily present a deposit of undissolved phosphates which is the product of their hydrolysis; when the concentration of these nitrates increases, this deposit first decreases and then completely dissolves due to a progressive increase of the concentration of free nitric acid in the solution.

The duration of layer formation, as judged by the period of hydrogen evolution (Fig. 2) and the volume of hydrogen evolved, increases considerably with the concentration of nitrates in the solution; this indicates that the rate of layer formation is considerably decreased. When the concentration of aluminum nitrates exceeds 60 g/liter, that of chromium nitrate 50 g/liter, and that of iron 30 g/liter, the duration of hydrogen evolution exceeds 2 hours.

The weight of the layer formed in the presence of aluminum, chromium, and iron nitrates is greatly decreased. The results obtained show that as the concentration of nitrates increases, the formation of the layer is hampered, probably by the liberation of a considerable amount of free nitric acid.

As the concentration of nitrates becomes very high the loss of weight of the original samples greatly increases, and for the different nitrates the weight loss increases in an increasing order from aluminum to iron nitrate; it must be noted that the acidity of the solution, and consequently its etching capacity, increase in the same order.

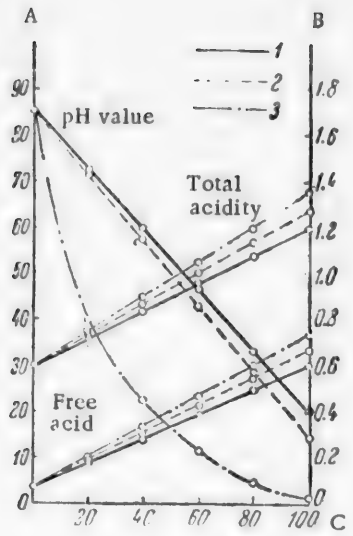

Fig. 1. Effect of the concentration of ammonium (1), chromium (2), and iron (3) nitrates on the acidity of the solution. A) Quantity of 0.1 N sodium hydroxide solution (ml). B) Value of pH. C) Concentration of nitrate (g/liter).

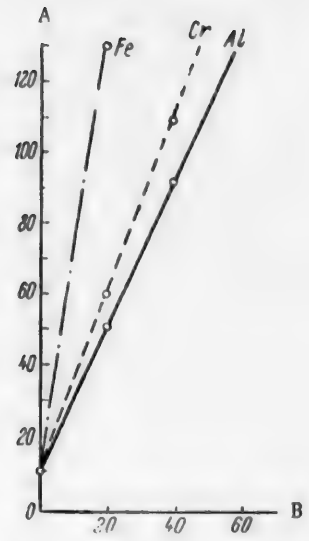

Fig. 2. Effect of the concentration of ammonium, chromium, and iron nitrates on the duration of hydrogen evolution. A) Duration of hydrogen evolution (min). B) Concentration of nitrate (g/liter).

In the presence of aluminum the color of the phosphate layer becomes gray. In the presence of chromium nitrate the layer acquires a green color characteristic of chromium compounds; this indicates that the nitrates not only affect the duration of the formation of the protective layer but also intervene in its formation. Iron nitrate leads to the formation of a predominantly black layer.

Aluminum, chromium, and iron nitrates contribute to the formation of a smooth phosphate-oxide layer. When the concentration of these nitrates increases, the microrelief of the layer becomes irregular and etched metal appears in isolated areas of the surface.

The protective properties of the layers decrease sharply as the concentration of the nitrates increases. The considerable amount of free nitric acid formed in the solution as the result of strong hydrolysis of the nitrates of trivalent metals increases the solubility of phosphates forming the layer. Under these conditions it becomes difficult to produce surface layers to protect the metal against corrosion.

Effect of nitric acid. These results as well as the results of the investigation made earlier [1, 2] show that the effect of nitrates of mono-, bi-, and trivalent metals on the process of formation and properties of the phosphate layer differ according to the nature of the cation of the nitrate introduced into the phosphatating solution.

We have explained this difference in the effects of the nitrates [1] by the difference in the capacity of the salts to become hydrolyzed, with liberation of free nitric acid, which modifies the process of formation and properties of the phosphate layer.

In order to verify this explanation we investigated the process of formation of phosphate layers in the presence of nitric acid (specific gravity 1.39) which was introduced into the solution as free nitric acid. The results of the investigation are summarized in the table.

The results in the Table show that nitric acid has an important effect on all the factors affecting the formation and properties of phosphate layers. The changes registered due to the presence of nitric acid are analogous to those induced by hydrolyzed nitrates. When the concentration of hydrolyzed nitrates or nitric acid increases, the acidity of the solution gradually increases, the rate of layer formation first increases and then decreases, the weight of the layer gradually decreases, a phosphate-oxide layer is formed, the surface of the layer becomes irregular, and the protective properties of the layer decrease.

Effect of the Concentration of Nitric Acid on the Formation Process and Properties of the Phosphate Layer

Concentration of nitric acid (g/liter)	Acidity of the solution (ml of 0.1 N solution of NaOH)		value of pH	Duration of layer formation		Change in weight of samples (g/m^2)	Surface irregularity (structure) and color of layer	Test in a 3% solution of sodium chloride	
	total acidity	free acid		duration of hydrogen evolution (min.)	volume of hydrogen evolved (ml/m^2)			duration of test up to beginning of corrosion (hr)	loss of weight ($g/m^2 \cdot hr$)
—	30*	4	1.69	10	2184	21.35	Usual surface irregularity, dark gray	102	0.0057
0.5	31.2	4	1.65	8	1632	17.38		73	0.0178
1.0	32.6	4.5	1.12	3	749	8.17		42	0.0287
1.5	33.9	4.8	0.93	1	288	1.54		27	0.0354
2.0	35.4	5.3	0.78	12	2738	— 1.86	Areas of smooth dark-blue phosphate oxide layer.	6	0.0436
3.0	37.8	6.7	0.52	31	4916	— 6.74		3.5	0.0455
4.0	40.6	9.2	0.27	58	7408	—12.15	Areas of metal eaten away, predominantly black.	1	0.0479
5.0	43.7	12.5	0.12	99	11124	—35.62		0.5	0.0488
6.0	46.9	17.5	0.03	Over 2 hrs.	39826	—89.13	Surface of metal eaten away.	—	—

*Control experiment.

Consequentlv the effects of hydrolyzed nitrates and nitric acid on the process of formation and properties of the phosphate layer are completely analogous.

Mechanism of the Effect of Nitrates on the Rate of Formation of Phosphate Layers

According to the existing theories the accelerating effect of nitrates on the formation of phosphate layers can be explained by the oxidizing action (depolarization of hydrogen evolved) due either directly to nitrates, or rather to NO_3' ions [3], or to the reduction of nitrates by nitrites, or NO_2' ions [4]. Therefore we could expect that all nitrates should accelerate the formation of phosphate layers. However, our results show that only certain groups of nitrates accelerate the formation of phosphate layers. The majority of nitrates of bivalent, and especially trivalent metals, considerably slow down the formation of phosphate layers. Sodium and potassium nitrates have no effect on the process of phosphate-layer formation [1]. Such differences in the effect of nitrates on the duration of layer formation have not been explained in the literature.

The variation of the period of layer formation as a function of the concentration of nitrates cannot be explained on the basis of the existing theory, and in fact contradicts it. The effect of calcium and strontium nitrates is characteristic: the rate of layer formation first increases and then decreases as their concentration in the solution increases [2].

The analysis of the experimental data obtained shows that the cause of the difference in the effect of nitrates on the duration of layer formation can be completely explained if one assumes that nitric acid formed in the solution as the result of hydrolysis of nitrates has a decisive effect on the rate of layer formation. Since the salts have different tendencies toward hydrolysis different amounts of nitric acid are formed in the solution. Therefore the effect of nitrates manifests itself differently with respect to the rate of formation and properties of the phosphate layers.

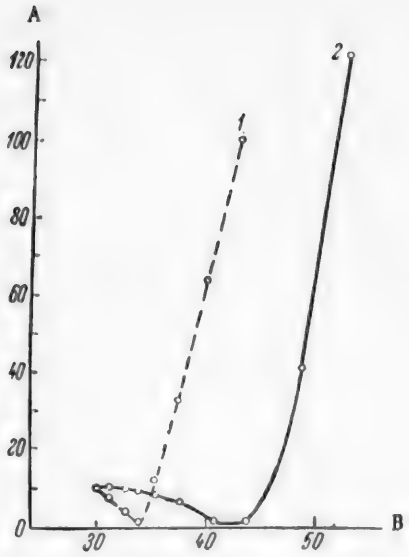

Fig. 3. Effect of nitric acid and nitrates on the duration of the formation of the phosphate layer. A) Duration of layer formation (min). B) Acidity of the solution (ml of 0.1 N NaOH). 1) Nitric acid, 2) nitrates.

The assumption that nitric acid has a decisive effect allows us also to explain the character of the relationship between the rate of layer formation and the concentration of nitrates. The existence of a minimum on the curves representing variation of the rate of layer formation as a function of concentration of nitrates (Communication 2 [2], Figs. 6 and 7) shows that under the effect of nitric acid produced by hydrolysis two opposite factors compete in their effects on the rate of layer formation.

One of these factors is the oxidizing action of nitric acid, which intensifies the cathodic process and leads to the increase of the rate of layer formation.

The second factor is the acidity of nitric acid. As the acidity of the solution increases, formation of the layer becomes more difficult and the rate of its formation decreases, since the solubility of phosphates in nitric acid increases with the concentration of the acid. According to the amount of nitric acid in the solution, one of these predominates and the predominance of that factor leads either to an increase or decrease of the rate of layer formation.

Our investigations showed that the duration of layer formation in the presence of nitrates varies regularly with the concentration of the acid in the solution. In the presence of nitrates which do not undergo hydrolysis (Na, K) the acidity of the solution and the rate of layer formation remain unchanged. Moderately hydrolyzed nitrates (NH_4, Mn, Zn, Cd) only slightly increase the acidity of the solution and therefore increase the rate of layer formation. Strongly hydrolyzed nitrates (Al, Cr, Fe) considerably increase the acidity of the solution and consequently slow down the rate of layer formation.

Free nitric acid introduced into the solution has an analogous effect on the rate of formation of phosphate layers. For low concentrations of acid the rate of layer formation increases, while the rate of layer formation decreases when the acidity increases.

There is a complete analogy between the effect of nitric acid and that of hydrolyzed nitrates on the process of layer formation. The shape and position of the curves presented in Fig. 3 illustrate the analogous effect of nitric acid and hydrolyzed nitrates; these curves are drawn on the basis of the data obtained for the variation of the period of layer formation as a function of the acidity of the solution induced by nitrates (at a concentration of 100 g/liter) and of free nitric acid (results summarized in the table).

The shape of these curves and the presence of a distinct minimum confirm our assumption that the effect of nitric acid on layer formation is the result of the effects of two opposite factors induced by this acid.

Thus we may consider that our hypothesis [1] was confirmed experimentally; according to this hypothesis the change of the duration of phosphate-layer formation and of other factors under the effect of nitrates is due to nitric acid formed as the result of hydrolysis of the salts in the phosphatating solution.

The nitrates having the optimum effect have been chosen for practical applications. Thus zinc nitrate, contrary to other nitrates (NH_4, Mn, and Cd), accelerates the rate of layer formation 10-12 times without decreasing the protective properties of the phosphate layer. Therefore, we have chosen this salt for use in a new accelerated method of phosphatation of metals [5, 6].

The addition of calcium, strontium, and barium nitrates to the solution of primary phosphates (Fe, Mn, and Zn) leads to the formation of a new type of phosphate-oxide layer which provides a relatively high degree of protection and is decorative even when its thickness is small. These properties of phosphate-oxide films were the basis for the development of an industrial process (alkali-free oxidation) for the protection of steel [5, 6] and zinc [7].

The theory of the formation of phosphate layers developed on the basis of our results shows that the mechanism of this layer formation is controlled essentially by the supersaturation of the solution in the reaction zone; experimental results confirming this theory allowed us to develop a third type of method of protecting metals against corrosion, namely cold phosphatation. This method consists of using high concentrations (100-300 g/liter) of primary phosphate (Fe, Mn, Zn) and makes it possible to obtain phosphate layers either by immersing the metal in the solution or, in the case of large structures which cannot be submerged (ships, for example), by application of the solution to the surface [6, 9].

SUMMARY

1. Nitrates of trivalent metals (Al, Cr, and Fe) added to the solution of primary phosphates considerably increase its acidity and slow down the process of formation of the phosphate layer, and also decrease the weight of the layer, its thickness, and its resistance to corrosion.

2. As the concentration of nitric acid increases, its effect on the process of formation and properties of the phosphate layer is qualitatively analogous to that of hydrolyzed nitrates.

3. The difference in the effect of different nitrates on the rate of formation and properties of the phosphate layer is due to the different amounts of nitric acid formed in the solution as the result of different degrees of hydrolysis of these nitrates.

4. The results of our investigation allowed us to develop three new methods of protecting metals against corrosion: accelerated phosphatation, formation of phosphate-oxide layers (alkali-free oxidation), and cold phosphatation; these three methods of protection have found practical applications in different branches of industry.

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SOLUBILITY OF HYDROGEN IN STEEL AT HIGH TEMPERATURES AND PRESSURES*

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To our knowledge there does not exist reliable data on the solubility of gases in metals at high pressures and temperatures. A number of investigators [1-5] have made experiments within a wide range of temperatures but at pressures not exceeding 1.5 kg/cm^2. The majority of data concerning solubility are relative to pure metals (iron, nickel, palladium) or double alloys; there are very few data concerning the solubility of hydrogen in carbon steel and low alloyed steels at high temperatures and pressures.

The solubility of gases in metals at high temperatures and pressures, particularly the solubility of hydrogen, is of great theoretical importance in the investigation of a number of problems relative to metallurgy, the physics of metals, and the corrosion of metals.

Materials Investigated and Method of Investigation

The chemical composition of the steels investigated is given in Table 1. In order to investigate the effect of alloyed elements on the solubility of hydrogen we used steels containing about 0.2% C with additions of chromium, vanadium, and titanium; as a standard of comparison we used steel No. 20.

TABLE 1

Chemical Composition of Steels Investigated

Type of steel or smelting No.	Chemical composition (%)										
	C	Si	Mn	Ni	S	P	Cr	Ti	W	V	Mo
20	0.22	0.32	0.60	0.10	0.038	0.007	0.12	—	—	—	—
1Cr18Ni9Ti	0.09	0.65	1.20	9.10	0.025	0.003	18.40	0.4	—	—	—
2Cr18Ni9	0.20	0.70	1.30	9.60	0.020	0.003	18.50	—	—	—	—
2Cr13	0.19	0.68	0.50	0.45	0.030	0.005	12.90	—	—	—	—
12Cr7CMoTi	0.12	0.60	0.55	0.23	—	—	7.00	0.44	—	—	0.50
15Cr12VMoF	0.15	—	—	—	—	—	12.70	—	0.6	0.18	0.48
№ 1	0.20	0.25	0.39	0.19	0.022	0.001	3.05	—	—	—	—
№ 2	0.18	0.26	0.39	0.18	0.022	0.002	5.93	—	—	—	—
№ 3	0.17	0.22	0.43	0.21	0.034	0.002	8.62	—	—	—	—
№ 4	0.16	0.20	0.46	0.20	0.034	0.001	—	0.48	—	—	—
№ 5	0.18	0.14	0.50	0.19	0.035	0.002	—	—	—	0.48	—

*Work begun under the guidance of Professor V. V. Ipatiev.

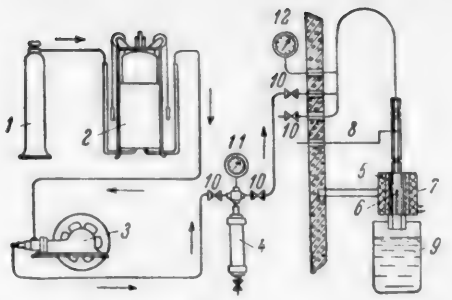

Fig. 1. Diagram of the apparatus for saturating metals with hydrogen. 1) Tank, 2) gas container, 3) compressor, 4) high-pressure tank, 5) autoclave, 6) sample, 7) furnace, 8) release lever, 9) water tank, 10) stopcocks, 11) and 12) manometers.

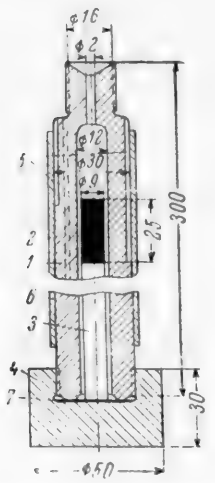

Fig. 2. Autoclave for saturating samples with hydrogen. 1) Body, 2) sample, 3) insert, 4) blind flange, 5) channels, 6) housing, 7) copper gasket.

To investigate the effect of the type of crystal lattice on the solubility of hydrogen, we used alloyed steels of the austenitic and ferrite-martensite class, widely used in technology necessitating high temperatures and pressures. All the steels were annealed before testing. In all tests we used technically pure hydrogen prepared by the iron vapor method.

The tests were made on samples 9 mm in diameter and 25 mm long. It is well known that a large part of hydrogen absorbed at high temperatures and pressures is released to the surrounding medium during slow cooling and relief of pressure. Consequently the extraction of hydrogen from metal cooled under these conditions cannot give the real value of the solubility of hydrogen in the metal. Therefore in this work we saturated the samples with hydrogen in a special apparatus which made it possible to cool the samples from high temperatures to room temperature without relieving the pressure. At room temperature the diffusion of hydrogen from steel is very small and the loss of hydrogen is reduced to a minimum if one extracts hydrogen from the saturated samples immediately after cooling.

Figure 1 represents the diagram of the apparatus used for the saturation of steels with hydrogen. From the tank, 1, hydrogen passes into the gas container, 2. From the container the gas passes into a five-step compressor, 3, which compresses hydrogen in the container, 4, up to 1000 kg/cm^2. From this container, 4, the hydrogen moves through high pressure conduits into the autoclave, 5, containing the sample, 6. The autoclave, 5, is placed in the electric furnace, 7, where it is heated to the desired temperature.

After the sample is maintained in the autoclave for a period of time sufficient for saturation (a period determined by preliminary experiments) the lever, 8, is moved without releasing the pressure and the autoclave, 5, falls into the tank, 9, filled with water and ice. Then the pressure is released and the sample removed from the autoclave.

Figure 2 represents the diagram of the autoclave. The body, 1, which is made of 1Cr18Ni9Ti steel, contains the sample, 2, and the inlay, 3, used to fix the sample in the center of the autoclave. The bottom of the autoclave is sealed with a blind flange, 4, while the top is connected with the high pressure line. There are three channels in the autoclave, 5, for thermocouples, which are held in position by a housing, 6.

The rate of cooling of the hydrogenated samples is the most important factor of the testing method. Therefore it was necessary to check the rate at which the metal in the autoclave cooled when the autoclave was plunged into the water. To determine this rate of cooling, thermocouples were welded to samples which were heated to 500°C in the autoclave. After a given time at this temperature the autoclave, with the samples at atmospheric pressure, was plunged into the water. This rate of cooling is represented in Fig. 3. Thus the steel under investigation cools at the same rate, which confirms the correctness of the proposed method of investigating the solubility of gases in metals.

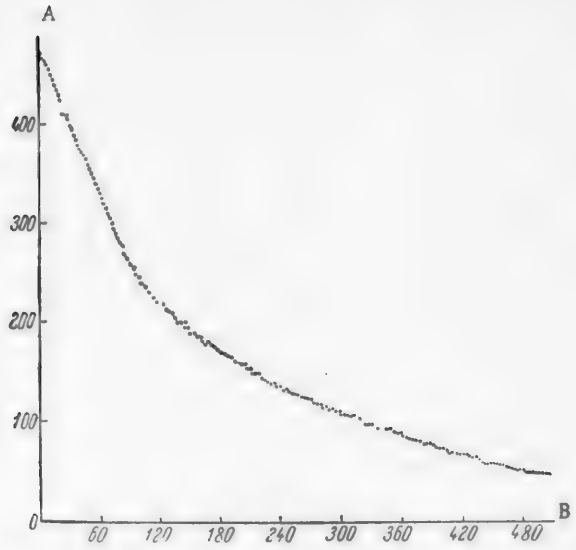

Fig. 3. Rate of cooling of samples. A) Temperature (°C). B) Time (sec).

TABLE 2

Solubility of Hydrogen in Certain Steels at a Temperature of 500° and Pressure of 100 kg/cm²

Type of steel or smelting No.	Test No.	Duration of saturation (hrs)	Hydrogen content (ml/100 g steel)	Test of steel or smelting No.	Test No.	Duration of saturation (hrs)	Hydrogen content (ml/100 g steel)
20	1	11	6.80	№ 1	1	41	3.40
	2	13	7.6		2	45	3.51
	3	18	7.8		3	70	3.53
1Cr18Ni9Ti	1	42	27.30	№ 2	1	41	3.30
	2	65	29.50		2	45	3.31
	3	90	30.00		3	70	3.32
2Cr18Ni9	1	44	33.41	№ 3	1	41	3.80
	2	55	34.80		2	45	3.80
	3	92	35.00		3	70	3.81
2Cr13	1	42	4.18	№ 4	1	20	4.50
	2	51	4.37		2	45	7.40
	3	71	4.37		3	76	7.42
12Cr7CMoTi	1	17	3.92	№ 5	1	21	8.30
	2	42	3.98		2	48	16.80
	3	50	4.00		3	90	17.00
15Cr12VMoP	1	17	5.15				
	2	42	5.16				
	3	50	5.18				

During the extraction of hydrogen• from the different steel samples it was observed that the rate of evolution of the gas is different for different steels. For example, in the case of alloyed steels 1Cr18Ni9Ti and 2Cr18Ni9 of the austenitic type the evolution of hydrogen resulting from extraction at 550°C continues for 19-20 hours, while for all the other steels in Table 1 the evolution stops after 2 hours. Figure 4 shows the rate of hydrogen evolution at 550°C for several steels saturated with hydrogen at 500°C under a pressure of 100 kg/cm².

• Hydrogen was evolved from the samples by the method of heating the metal under vacuum [4].

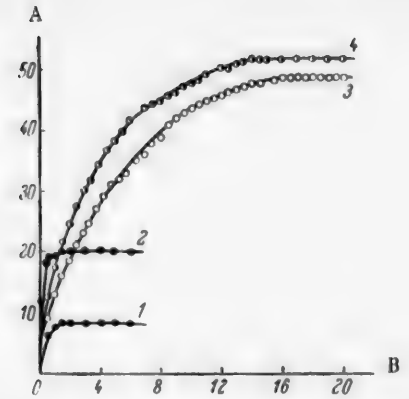

Fig. 4. Rate of hydrogen evolution. A) Pressure of evolved hydrogen (in mm of mercury). B) extraction time (hrs). Type of steel: 1) 2Cr13, 2) Steel No. 20, 3) 1Cr18Ni9Ti, 4) 2Cr18Ni9.

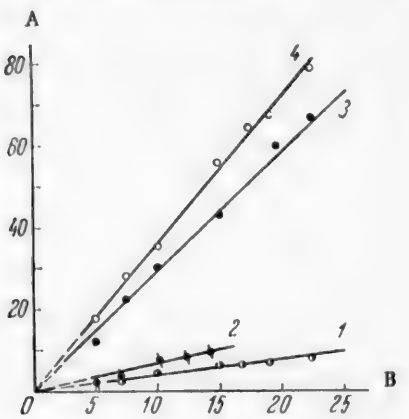

Fig. 6. Solubility of hydrogen as a function of pressure at t = 500°C. A) Quantitative of hydrogen dissolved (ml/100 g steel). B) Hydrogen pressure $\sqrt{P}$ (kg/cm^2). Type of steel: 1) 2Cr13, 2) Steel No. 20, 3) 1Cr18Ni9Ti, 4) 2Cr18Ni9.

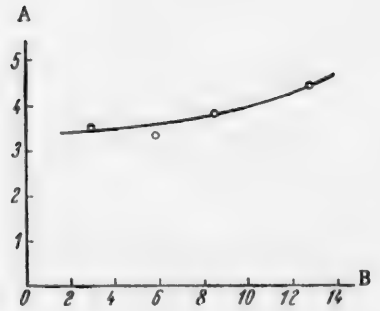

Fig. 5. Solubility of hydrogen as a function of the chromium content of steel. (P = 100 kg/cm^2, t = 500°C). A) Quantity of hydrogen dissolved (ml/100 g steel). B) Chromium content (%).

RESULTS OF THE INVESTIGATION

To determine the solubility of hydrogen in different steels (Table 1) and to elucidate the effect of different alloyed elements we performed a series of experiments at 500°C under a pressure of 100 kg/cm^2. We subjected each type of steel to three experiments, each one of which corresponded to a different period of saturation, so as to determine the solubility limit of the gas in the metal.

The results of these experiments are shown in Table 2; the solubility of hydrogen is greater in carbon steels containing 0.48% vanadium than in ordinary carbon steel.

The increased solubility in steel containing vanadium can be explained by the increase of the parameters of the crystal lattice, occurring during the formation of solid solutions, as the result of the difference between the atomic diameters of vanadium and iron.

The addition of up to 13% chromium to a steel containing 0.2% C induces only an insignificant increase of solubility of hydrogen (Table 2, Fig. 5).

Chromium, which forms replacement solid solutions with iron, is practically without effect on the parameters of the crystal lattice (the difference between the atomic diameters of chromium and iron is 1%). It is probable that the presence of chromium in steel has very little effect on the solubility of hydrogen.

Alloyed steels of the austenitic type, 1Cr18Ni9Ti and 2Cr18Ni9, dissolve about 4 times more hydrogen than carbon steel No. 20 and about 6-7 times more than alloyed steels of the ferrite-martensite class, 2Cr13, 12Cr7CMoTi and 15Cr12VMoP (Table 2).

It seems to us that this can be explained by the difference in the types of crystal lattices (which is in agreement with the results obtained by Morozov [3] for α and γ-iron) and by the fact that in these steels chemical compounds between nickel and hydrogen may be formed.

To decide whether the law of solubility of gases in metals ($V = K\sqrt{P}$) can be extended to the region of high pressures, we performed experiments at 500°C at pressures varying from 25 to 500 kg/cm^2 on 1Cr18Ni9Ti, 2Cr18Ni9, 2Cr13 and carbon steel No. 20. The results of these experiments are shown in Table 3. The same results are given

TABLE 3

Solubility of Hydrogen in Steel at Temperatures of 500° and Pressures of 25-500 kg/cm²

Type of steel	Test No.	Hydrogen pressure (kg/cm²)	Quantity of hydrogen dissolved (ml/100 g steel)	Solubility of hydrogen (data calculated in ml/100 g steel)	
				according to Schenck [2]	according to Siverts [1]
20	1	25	1.80	—	—
	2	50	3.57	—	—
	3	100	7.80	7.64	12.3
	4	150	8.30	9.35	15.0
	5	200	9.44	10.80	17.7
1Cr18Ni9Ti	1	25	12.20	—	—
	2	55	22.30	—	—
	3	100	30.00	—	—
	4	225	42.70	—	—
	5	380	59.50	—	—
	6	500	66.50	—	—
2Cr18Ni9	1	25	17.50	—	—
	2	55	28.00	—	—
	3	100	35.00	—	—
	4	220	55.50	—	—
	5	300	64.20	—	—
	6	360	67.20	—	—
	7	500	78.50	—	—
2Cr13	1	50	2.52	—	—
	2	100	4.40	—	—
	3	225	6.20	—	—
	4	290	6.20	—	—
	5	360	6.89	—	—
	6	500	8.00	—	—

in Fig. 6 in coordinates representing the solubility of hydrogen (in ml/100 g steel) and $\sqrt{P}$; these curves show that for all the steels investigated the solubility of hydrogen is directly proportional to the the square root of the pressure.

The experimental results (Table 3) differ from the values obtained as the result of extrapolation of the data of solubility obtained by Sieverts[1], while they are in good agreement with more recent data obtained by Schenck [2].

The results of our experiments allow us to conclude that the law of solubility of gases in metals expressed by the formula $V = K\sqrt{P}$ is apparently valid also for high pressures of gases in the case of pure metals as well as in the case of different types of steels.

SUMMARY

1. We have studied the solubility of hydrogen in different steels at 500°C at different pressures up to 500 kg/cm²; it was found that the solubility of hydrogen at 500°C and 100 kg/cm² is 4 times greater in the austenitic steels 1Cr18Ni9Ti and 2Cr18Ni9 than in steel No. 20, and about 6 times greater than in alloyed steels of the ferrite-martensite class (2Cr13, 12Cr7CMoTi, and 15Cr12VMoP).

2. Our experiments have confirmed the fact that for steels No. 20, 2Cr13, 1Cr18Ni9Ti and 2Cr18Ni9Ti at 500°C and at pressures up to 500 kg/cm² the law of solubility of gases in metals, $V = K\sqrt{P}$, holds.

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THE ACTION OF FUSED NITRATE–NITRITE MIXTURE AND ITS COMPONENTS ON MOLYBDENUM, TUNGSTEN, ZIRCONIUM, TANTALUM AND NIOBIUM

E. I. Gurovich and G. P. Shtokman

In earlier investigations [1] we showed that the corrosion behavior of steels in fused nitrate–nitrite mixture (composition 53% KNO_3, 40% $NaNO_2$ and 7% $NaNO_3$) depends to a large extent on the presence of other alloying elements in the steels. Chromium, for instance, makes steel less resistant to corrosion due to development of alkalinity in the melt after more or less prolonged heating. Additions of nickel to steels lead to improved resistance in the melt in full agreement with our investigations of the action of nitrates on metals [2]. Steels alloyed with niobium or vanadium were more or less stable only up to 550°. Steels containing molybdenum and tungsten had extremely poor corrosion resistance in fused nitrate–nitrite mixture.

We wished to determine the effect of certain steel-alloying components on the stability of these steels in fused nitrate–nitrite mixture or in melts containing components of this mixture. For this purpose we investigated the behavior of such media on potential and actual alloying additives such as molybdenum, tungsten, zirconium, tantalum and niobium.

We tested the action on the above metals of a fused mixture of KNO_3, $NaNO_3$ and $NaNO_2$ at various temperatures and for various periods of immersion in the melt.

EXPERIMENTAL

Tests on the above metals were carried out in quartz containers. Specimens of the metals were set up at the bottom of the vessels in such a manner that they were uniformly washed by the melt during the test period.

Degree of Purity of the Metals Tested

Molybdenum	99.96% (traces of C, O_2 and N_2)
Tungsten	99.1% (traces of C, SiO_2)
Zirconium	99.9% (traces of Hf, Zn)
Tantalum	99.8% (traces of Nb, O_2)
Niobium	99.6% (traces of C, Ta, O_2)

Molybdenum was tested in nitrate–nitrite mixture at temperatures of 250, 300, 350 and 400°. The duration of the tests ranged from 5 min to 1 hr (5, 10, 15, 25, 30 and 60 min). Similar tests were applied in melts of KNO_3, $NaNO_3$ and $NaNO_2$ at temperatures of 300, 350 and 400° (depending on the melting point of the component, the lowest test temperature was selected).

Solution isotherms of molybdenum in melts of the above salts are plotted in Fig. 1.

Inspection of the curves indicates that solution of molybdenum in the melts is intensified with rising temperature and with duration of testing. We see, for example, from the 350° curves that the fused salt with the greatest action on molybdenum is $NaNO_3$ (rate of corrosion about 860 $g/m^2 \cdot$ hour). This is followed by $NaNO_2$ (about 700 $g/m^2 \cdot$ hour); the melt of the mixture of these two salts occupies the third place (about 550 $g/m^2 \cdot$ hour); finally we have KNO_3 as the salt with the least action on molybdenum (about 220 $g/m^2 \cdot$ hour).

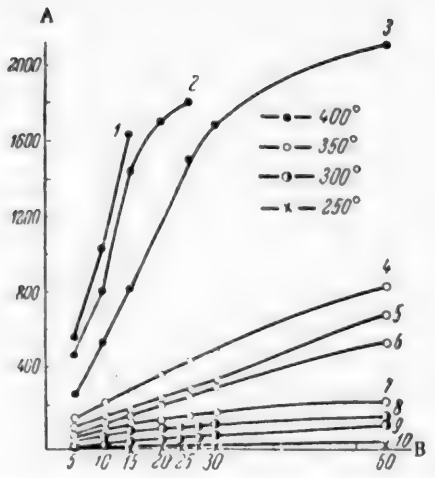

Fig. 1. Solution isotherms of Mo in fused salts. A) Losses by corrosion (in g/m^2); B) time in min. 1) $NaNO_2$, 2) $NaNO_3$, 3) mixture, 4) $NaNO_3$, 5) $NaNO_2$, 6) mixture, 7) KNO_3, 8) mixture, 9) $NaNO_2$, 10) mixture.

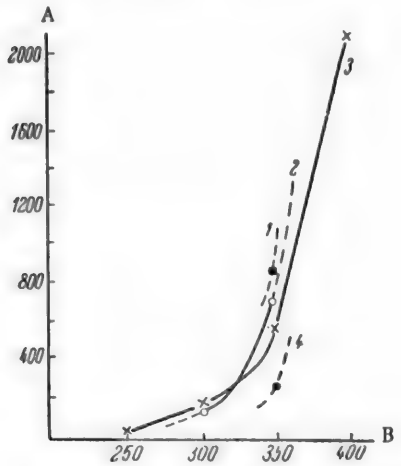

Fig. 2. Solution polytherms of Mo. A) Losses from corrosion (in $g/m^2 \cdot$ hour); B) temperature (° C). 1) $NaNO_3$, 2) $NaNO_2$, 3) mixture, 4) KNO_3

We see from Fig. 1 that in melts of $NaNO_3$ and $NaNO_2$ the tests had to be terminated at 400° due to complete oxidation of the specimen considerably in advance of the programmed period. We know that molybdenum is strongly oxidized in the air at temperatures above 400° [3, 4]. In our case the oxidation process is evidently effected at the expense of the oxygen of one salt or the other. This intensification of molybdenum oxidation with rising temperature is illustrated by the curves of Fig. 2 (polytherms of solution of molybdenum).

Exposure of molybdenum at 450° to fused nitrate—nitrite mixture led after only two min to ignition and to complete combustion of the specimen. The salt of molybdic acid was detected afterwards in the melt.

On the basis of chemical analyses of the salt melts after the tests and of analysis of the gas phase (due to the reaction during dissolution of molybdenum, the procedure was modified in this case by use of a sealed apparatus in order to enable trapping of the released gases), the process of interaction of molybdenum with melts of the above salts and their mixtures can be represented by the following equations:

$$2NaNO_3 + Mo \rightarrow Na_2MoO_4 + N_2 + O_2, \quad (1)$$

$$2NaNO_2 + Mo \rightarrow Na_2MoO_4 + N_2. \quad (2)$$

Analysis of the gas phase revealed the presence of nitrogen and oxygen. Oxides of nitrogen were only detected in a few cases and in the first seconds of the experiments.

After an experiment the melt has an alkaline reaction. Decomposition of Na_2MoO_4 to Na_2O and MoO_3 is possible.

Tests on molybdenum in fused nitrates, nitrites and their mixture showed very clearly that steel alloyed with molybdenum should not be used for operations with the above fused salts unless molybdenum forms with other components of the steel more stable solid mixtures or chemical compounds. In the steels that we previously tested [1] such stable molybdenum compounds were evidently not formed.

Tungsten was tested in fused nitrate—nitrite mixture at 200, 250, 300 and 350°; the test period was 1 hr. Attempts to carry out tests at 400° led to ignition and complete burning of the specimen. At the same time the tungsten oxidation reaction raised the temperature from 400° to about 700° (the temperature of the melt was measured by an immersed thermocouple shielded by a thin quartz test tube).

We see from Fig. 3 that corrosion of tungsten in nitrate—nitrite melt increases with rising temperature. At 200° it is 5.27 $g/m^2 \cdot$ hr while at 350° it reaches the enormous value of 1160 $g/m^2 \cdot$ hr.

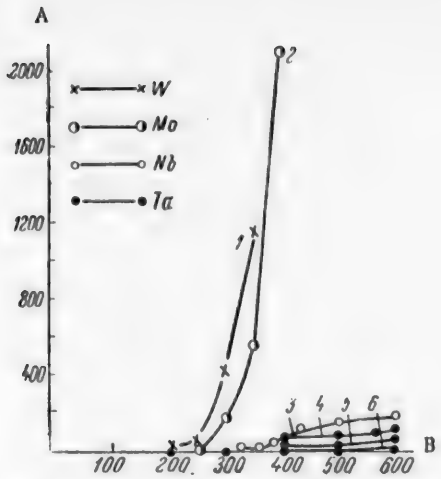

Fig. 3. Solution polytherms of W, Mo, Nb and Ta. A) losses by corrosion (in $g/m^2 \cdot hr$); B) temperature (° C). 1) mixture, 2) mixture, 3) $NaNO_3$, 4) $NaNO_2$, 5) $NaNO_3$, 6) mixture.

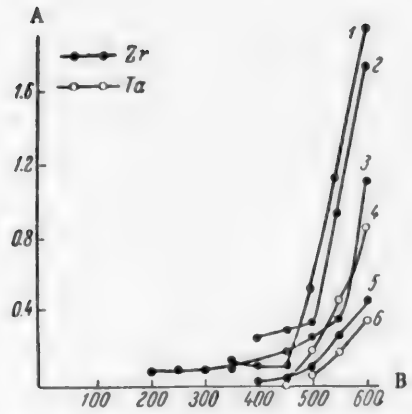

Fig. 4. Solution polytherms of Zr and Ta. A) Losses by corrosion (in $g/m^2 \cdot hr$); B) temperature (° C). 1) $NaNO_3$, 2) KNO_3, 3) mixture, 4) $NaNO_3$, 5) $NaNO_2$, 6) mixture.

Chemical analysis of the melt after an experiment and analysis of the gas phase indicates that tungsten can react with the melt in accordance with the equations

$$2NaNO_3 + W \rightarrow Na_2WO_4 + N_2 + O_2, \quad (3)$$

$$2NaNO_2 + W \rightarrow Na_2WO_4 + N_2. \quad (4)$$

The results show that tungsten is even less desirable than molybdenum as an alloying component in steel.

Tests on the reaction of tantalum with melts of nitrate–nitrite mixture and its components were carried out at 200, 250, 300, 350, 400, 450, 500, 550 and 600°. Immersion periods in each series were 15, 30 and 60 min; for the $NaNO_3$ melt the immersion period was the same but the test temperatures were 450, 500, 550 and 600°; for KNO_3 the immersion period was also the same but the test temperatures were 400, 450, 500, 550 and 600°; for $NaNO_2$ the immersion period was 60 min and the test temperatures were 400, 450, 500, 550 and 600°.

In nitrate–nitrite melt the losses of weight of the samples were extremely small up to 500°, but at higher temperatures they were 0.2-0.4 $g/m^2 \cdot hr$ (Fig. 4).

In $NaNO_3$ melt at 600° the losses by corrosion of tantalum were about 1.2 $g/m^2 \cdot hr$.

At the same temperature (600°) in KNO_3 melt the corrosion of tantalum increased to 5 $g/m^2 \cdot$ hr, while at lower temperatures it fell appreciably–to 0.4 $g/m^2 \cdot$ hr at 450°.

In $NaNO_2$ melt at 600° tantalum lost about 60 $g/m^2 \cdot hr$ by corrosion; at 450° the loss was about 8 $g/m^2 \cdot hr$.

After the tests the samples had a white film of tantalum oxide (Ta_2O_5), and the liberated gas contained nitrogen and oxygen; the melt was always alkaline after an experiment. In the light of these observations, the reactions during these tests might be represented by the equations:

$$2NaNO_3 + 2Ta \rightarrow Ta_2O_5 + Na_2O + N_2, \quad (5)$$

$$4NaNO_2 + 2Ta \rightarrow Ta_2O_5 + 2Na_2O + 2N_2 + O. \quad (6)$$

These investigations have shown that tantalum is considerably more stable in melts of nitrates and nitrites than are the previously tested metals. A steel alloyed with tantalum must therefore have greater resistance to corrosion in contact with fused nitrates, nitrites and their mixtures.

Figure 4 also shows the corrosion losses of zirconium which was tested both in nitrate–nitrite mixture and in melts of the separate components. In all cases the tests extended over 1, 2 and 6 hr at temperatures of 400 to 600°; in addition tests with nitrate–nitrite mixture were run at 200, 250, 300 and 350°.

Losses by corrosion in nitrate–nitrite mixture were 0.07 to 1.12 $g/m^2 \cdot hr$; for $NaNO_3$ they were 0 to 1.96 $g/m^2 \cdot hr$; for KNO_3 they were 0 to 1.75 $g/m^2 \cdot hr$; and for $NaNO_3$ they were 0 to 0.42 $g/m^2 \cdot hr$.

The possible reactions may be expressed by the equations:

$$4NaNO_3 + Zr \rightarrow ZrO_2 + 2Na_2O + 2NO_2 + N_2 + 2O_2, \quad (7)$$

$$4NaNO_2 + Zr \rightarrow ZrO_2 + 2Na_2O + 2NO_2 + N_2. \quad (8)$$

These reaction equations are supported by the alkaline reaction of the salts after the tests, by the liberation of oxides of nitrogen, nitrogen, and oxygen, and by the formation on the samples of films of different oxidation stages and ranging in color from blue to gray.

Zirconium can be recommended, in addition to tantalum, as an alloying additive to steels for use with nitrates and nitrites in the fused state.

Figure 3 contains, in addition to data for molybdenum, tungsten and tantalum, a plot of the loss of niobium by corrosion after exposure to a bath of sodium nitrate at temperatures of 350, 400, 450, 500 and 600°. Each of the tests extended over an hour.

Corrosion of niobium increases with rising temperature from 0.14 to 120 $g/m^2 \cdot hr$.

The specimens became covered with a white film of oxide (Nb_2O_5) during the tests, the melt afterwards had an alkaline reaction, and nitrogen came off during the tests. We can therefore represent the reaction of niobium with the fused salt by the equation

$$2NaNO_3 + 2Nb \rightarrow Nb_2O_5 + Na_2O + N_2 \quad (9)$$

On the basis of the results, the application of niobium as an alloying component must be limited to steels for use at a maximum temperature of 400°. Niobium has poor resistance above this temperature in fused nitrates, nitrites or their mixtures, although it is very much more resistant than molybdenum and tungsten.

SUMMARY

Of the metals tested, the least resistant in fused nitrates, nitrites and their mixtures is tungsten; next in order is molybdenum. The other metals that were tested are very much more resistant; in respect of stability they can be put in the order: zirconium (the most stable), tantalum, niobium. The last metal, however, is very much more resistant to corrosion than tungsten and molybdenum. The fused salts and their mixtures also differ in their reactivity towards each metal.

2. Molybdenum and tungsten should not be present as alloying components in steels that must come into contact with fused nitrates, nitrites and their mixtures. On the other hand the other metals tested can enter into the composition of steels intended for contact with the same salts at high temperatures.

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THE FORMATION AND STABILITY OF COLLOIDAL COMPOUNDS OF NICKEL IN THE ELECTROLYTE OF ELECTROLYZER BATHS

A. L. Rominyan and E. S. Kozich

The literature has often emphasized the important role of colloidal formations in the process of electrodeposition of nickel [1]. Formation of colloidal compounds of hydrated nickelous oxide or basic salts of nickel is considered, in particular, to be responsible for the "critical" pH value of the electrolyte above which the cathodic deposits acquire increased hardness [2]. Ultramicroscopic studies of nickel solutions have also led to the conclusion that even at extremely high pH values in the near-cathode film no colloidal structures are developed during electrolysis of nickel [3].

Potentiometric measurements have shown [4] that sparingly soluble compounds are formed in the nickel electrolyte at fairly low pH values, especially in presence of boric acid. It was then established that in the nickel electrolyte containing boric acid the sparingly soluble particles are nickel diborate—$2H_3BO_3 \cdot Ni(OH)_2$ [5], in a pure solution of nickel sulfate the particles are $3NiSO_4 \cdot 4Ni(OH)_2$, while at higher activities of the nickel sulfate and in dilute solutions the particles consist of $Ni(OH)_2$ [6] or $NiSO_4 \cdot 9Ni(OH)_2$ [7].

Examination of the processes taking place near the cathode show that in a nickel electrolyte the alkalinity imparted to the near-cathode film in some cases can reach,but not exceed,the value of acidity corresponding to the start of formation of solid phase [8].

We believe there is no doubt that under certain conditions colloid structures can be formed at the near-cathode film of electrolyte, as well as within the layer. The problem of the stability of the colloids in the electrolyte, however, has not previously been studied.

The relation between potentiometric titration data and the optical properties of the solution is also obscure. The existing method of control of the start of formation of solid phase by visual observation of the development of a Tyndall cone [4] is a sensitive indication of formation of solid phase but is inadequate for characterization of the stability of the colloidal compounds. In the present work we have therefore made use of the nephelometric method of Zhurin and Shoikhet [9] for study of the stability of the colloids.

We modified the method of Zhurin and Shoikhet in that the potentiometric titration of the electrolyte with alkali was performed directly in the cell of the Pulfrich nephelometer; also the turbidity (expressed as scale divisions) was measured during the experiment and not after completion of the titration and formation of deposit as in the procedure of Zhurin and Shoikhet. The pH was also measured during the experiment (with the aid of a glass electrode immersed in the cell). The reagents for the investigations were carefully purified beforehand.

Figure 1 contains plots of a series of measurements of the turbidity index and pH value during titration with alkali of nickel sulfate solutions (1 N $NiSO_4$) with addition of various amounts of boric acid. After addition of each portion of alkali, the solution was stirred mechanically until visual observation indicated no further change in turbidity. This stage was usually reached after several minutes.

These experiments show that when alkali is added to the electrolyte the initial turbidity either does not increase at all at first or increases to an insignificant extent. Subsequently the straight-line relation changes abruptly and the turbidity of the solution commences to increase. The inflection on the curve evidently marks the development in the solution of colloidal particles whose dimensions are such as to scatter rays of transmitted light. Comparison of the turbidity curves with the potentiometric titration curves shows that the colloidal

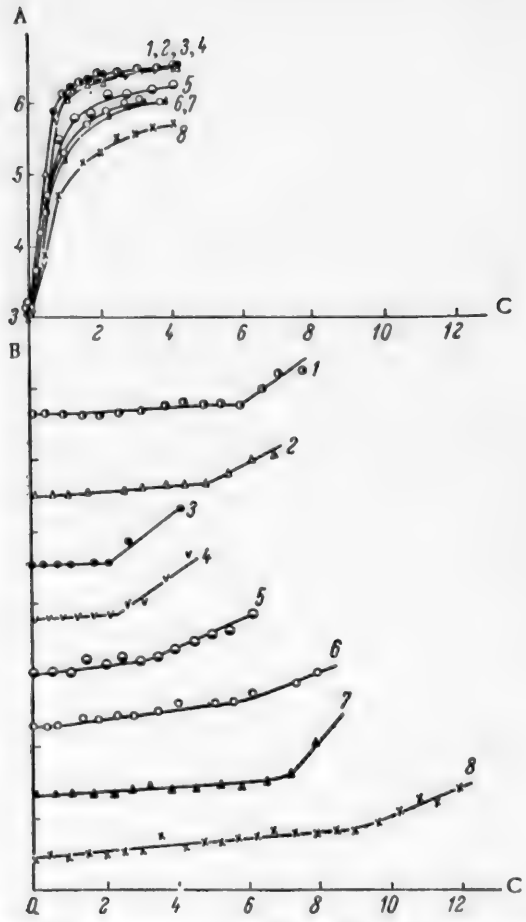

Fig. 1. Curves of turbidity index and potentiometric titration of nickel sulfate solution(30 g Ni/liter) containing various amounts of boric acid. A) pH value, B) divisions of nephelometer scale, C) quantity of 0.1 N NaOH solution (in ml). H_3BO_3 (in g/liter): 1) 0, 2) 2, 3) 2.5, 4) 3, 5) 5, 6) 8, 7) 12, 8) 20.

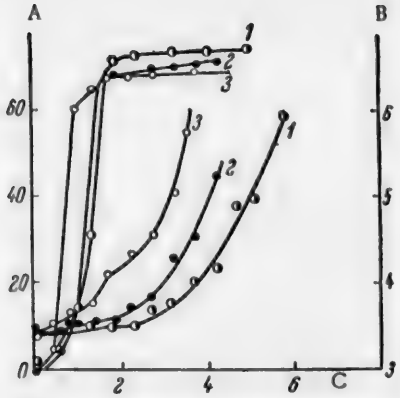

Fig. 2. Influence of concentration of sodium sulfate in electrolyte on stability of the colloidal particles. A) Scale divisions of nephelometer, B) pH value, C) quantity of 0.3 N NaOH solution (in ml). Na_2SO_4 (g/liter): 1) 100, 2) 50, 3) 0.

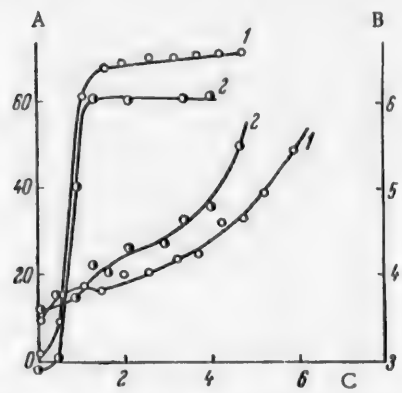

Fig. 3. Influence of sodium chloride concentration in electrolyte on stability of colloidal particles. A) Scale divisions of nephelometer, B) pH value, C) quantity of 0.3 N NaOH solution (in ml). NaCl (in g/liter). 1) 0, 2) 50.

particles of the solid phase are already formed on addition of 0.5-1 ml of alkali. We can accordingly assume that the continuation of the horizontal portion of the turbidity curves corresponds to the formation of micelles of such small size that they are not amenable to determination by the nephelometric method. The portion of the horizontal part of the turbidity curve starting from the point of commencement of development of colloidal particles and continuing up to the inflection of the turbidity curve consequently characterizes the degree of stability of the colloids.

A number of factors affect the stability of the micelles. To a very large extent the stability depends primarily on the boric acid concentration in the electrolyte. High boric acid concentrations increase the stability relative to the stability in boric-acid-free nickel solution. But the stability of the colloidal solution decreases sharply with decreasing boric acid concentration. In presence of 3-4 g H_3BO_3/liter the stability falls to a minimum which is lower than that in pure nickel sulfate solution. This minimum is probably caused by the isoelectric point lying at pH values equal to those of the start of formation of solid phase under these conditions.

In later series of experiments the influence of sodium sulfate and chloride on the stability of the micelles in nickel solution was studied. We see from Figs. 2 and 3 that sodium sulfate increases and sodium chloride

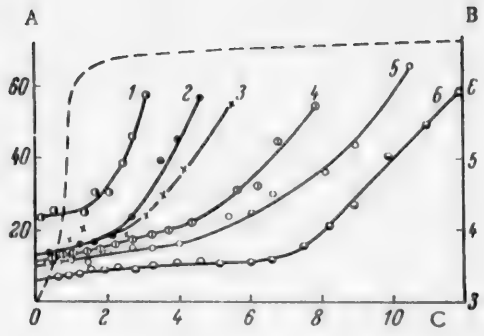

Fig. 4. Influence of organic additions on stability of the colloidal particles. Composition of electrolyte (in g/liter): Ni—40, NaCl—23.2, Na_2SO_4—47.9, H_3BO_3—0. The organic concentration was expressed as milligrams of carbon per liter of solution. A) Scale divisions of nephelometer, B) pH value, C) quantity of 0.3 N NaOH solution (in ml). Carbon (in mg/liter): 1—50, 2—38, 3—30, 4—20, 5—14, 6—8.

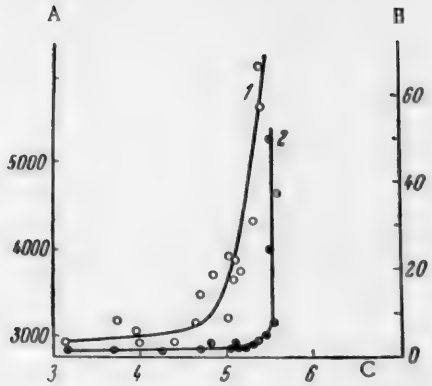

Fig. 5. Comparative curves of turbidity index of solution and internal stresses in cathodic deposits obtained from the same solution. Composition of solution (in g/liter): Ni—50, Na_2SO_4—40, NaCl—50. A) Value of P (in kg/cm^2), B) scale divisions of nephelometer; C) pH value at 50°. 1) Internal stresses, 2) turbidity.

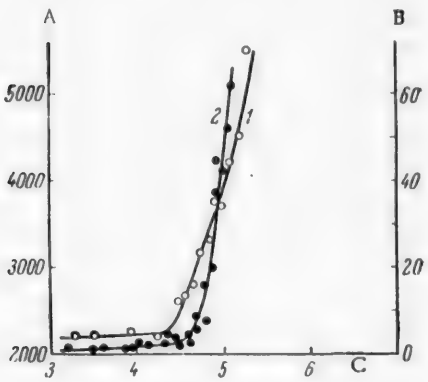

Fig. 6. Comparative curves of turbidity index of a solution and of hardness of cathodic deposits obtained from the same solution. Composition of solution (in g/liter): Ni—50, Na_2SO_4—40, NaCl—50, H_3BO_3—20. A) Value of P (in kg/cm^2), B) pH value at 50°, C) scale divisions of nephelometer. 1) Internal stresses, 2) turbidity.

decreases the stability of the colloidal particles. Very small additions of organic substances (an aqueous extract of wood shavings) reduce the stability to a considerable extent and coagulate the micelles (Fig. 4). Addition of the extract in quantity equivalent to 50 mg carbon/liter thus substantially reduces the stability to zero. This is characterized by the coincidence of the inflections of the curves of turbidity and pH values at the axis of the abscissas. The carbon content of the extract was determined in the electrolyte after a predetermined volume of extract had been added.

In later series of experiments we established a relation between the turbidity curves and the internal stresses. The latter were determined by the previously described method, using a contactometer [10], in the same solution in which the turbidity index had previously been determined. The curves obtained are presented in Figs. 5 and 6. In the absence of boric acid from the electrolyte the inflection on the internal-stresses curve was much higher than that on the turbidity curve (Fig. 5). This points to the formation in a pure nickel electrolyte of exceedingly fine colloidal particles which are intensively adsorbed by the cathodic deposit and increase the internal stresses in the deposit even before the particles are detected by the nephelometer. At cathodic potentials corresponding to electrolysis conditions, the zero discharge potential of the nickel surface is more positive than the cathodic potential, and therefore the surface of the nickel cathode is negatively charged.

Consequently the intensive adsorption by the cathode surface of the colloidal particles is evidence of their positive charge. Conversely, in presence of boric acid the inflections on the curves of turbidity and internal stresses are located at very similar pH values. This indicates that very fine colloidal particles are not adsorbed by the cathode surface (their charge is negative). Only after the particles have considerably increased in size and have consequently lost their aggregative strength does the phenomenon of their adsorption start to influence the growing cathodic deposit.

In conclusion we may note that the foregoing experiments provide an explanation of the discrepancies between our results [4] and those of Vozdvizhenskii [3] if we postulate that under the conditions of experiments with the ultramicroscope a stable colloidal system with very small micelles was formed.

SUMMARY

1. A study by the nephelometric and potentiometric methods of colloidal hydrated nickelous oxide or basic nickel salts obtained in a nickel solution when the latter is made alkaline revealed a considerable aggregative stability of the micelles in nickel sulfate solution. The stability of the colloidal system was also found to be influenced by boric acid, sodium sulfate and chloride, and an "organic" additive.

2. Comparison of nephelometric and contactometric results revealed that the sign of the charge on colloidal particles when nickel sulfate solution had been made alkaline in presence of boric acid was different from that in absence of boric acid.

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INVESTIGATION OF THE INFLUENCE OF ORGANOPOLYSILOXANE COATINGS ON THE ADHESION OF ICE TO VARIOUS SURFACES

K. A. Andrianov, B. V. Deryagin, N. N. Zakhavaeva, M. V. Sobolevskii and M. V. Talaev

By the term "ice formation" is understood the formation of ice coatings on surfaces under certain meteorological conditions or under conditions of use of refrigerating equipment.

The study of the processes of ice formation is of great practical interest in aviation, in the prevention of icing of electrical conductors exposed to atmospheric conditions, and for the operation of pipes in refrigerators, etc. Ice formation on aircraft is a serious hindrance to efficient working of air transport services. Ice formation on conductors is a frequent cause of breakage and can cause serious damage. Ice formation on pipes of refrigerators leads to interruption of operation. Other examples of the necessity of dealing with ice formation could be cited.

A study of the icing process requires a knowledge of the adhesion of ice to various surfaces and possible means of reducing its adhesion.

Several authors have occupied themselves with this problem. Some of them (Kobeko, Morei, Lebedev [1-3]) arrived at the conclusion that ice adhesion cannot be seriously reduced at surfaces by application of coatings of various hydrophobic substances.

Other workers have achieved considerable reduction of adhesion by application of silicone films to surfaces subjected to ice formation [4, 5].

We have investigated the adhesion of ice to various surfaces and have tested organopolysiloxane coatings for their adhesion-lowering ability.

EXPERIMENTAL

Test apparatus and method. The influence of polysiloxane coatings on the adhesion of ice to various surfaces was studied with a specially designed apparatus in which water filled into small glass cylinders was brought into contact with specimens of various materials and then frozen. The ice was then broken off from the specimens in a tangential direction and the shearing force was measured in g/cm^2. The main portion of the apparatus was a carriage which moved over a heavy metal plate. In the plate was a groove along which small spheres rolled and replaced the wheels of the carriage (Figs. 1 and 2). The carriage was moved by a small Warren motor at a speed of 2 cm/min. The carriage travelled with great uniformity (no jolts). On this carriage were placed four cylindrical cells with a diameter of 5 mm and a height of 7 mm. Over each cell on special holders was suspended a specimen in the form of a $1 \times 1 \times 0.5$ cm rectangular parallelepiped. Alternatively one specimen was arranged over the whole of the cells. The large specimen had dimensions of $2 \times 20 \times 0.5$ cm (Fig. 3). Various materials were used as specimens: rubber, duralumin, silicate (window) glass, organic glass (plexiglas). They were coated with a film of polysiloxane liquid whose antiicing properties were to be tested.

The cells were filled with water. The water had a convex meniscus of large curvature which extended above the edges of the cell. The specimens were brought into contact with the meniscus of the water. Small specimens were contacted with the cell from the 1×1 cm side, the larger ones from the 2×20 cm side.

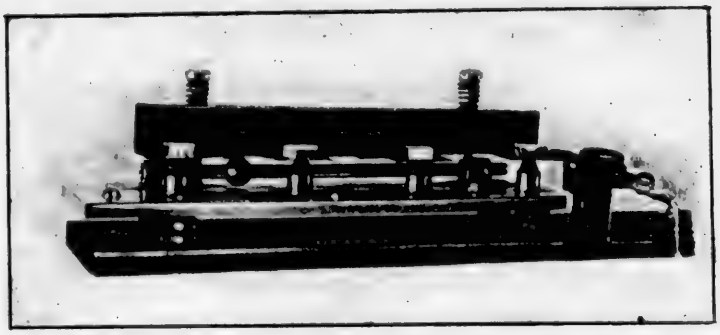

Fig. 1. Specimens of organic glass. Holders raised and specimens supported on them.

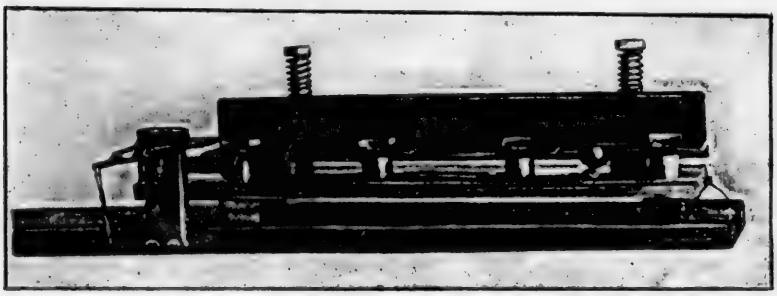

Fig. 2. Glass specimens. Specimen holders let down and specimens held on the glass surface of the cells.

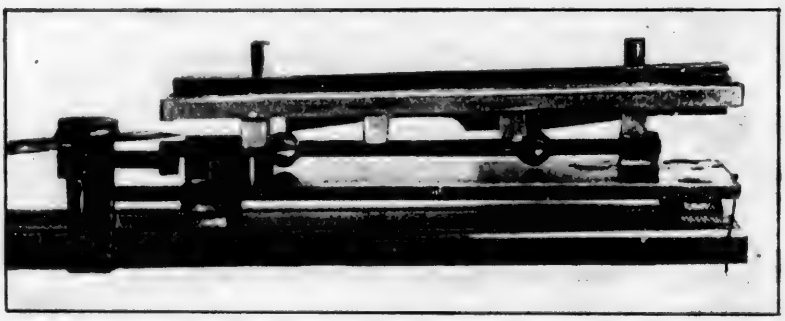

Fig. 3. Large specimen with ice cells frozen to it.

The surface of contact of water and specimen had the shape of a sphere with a diameter of 2-7 mm.

The carriage on the metal plate was put in a refrigerator whose temperature could be lowered to -20°. After the water had been converted into ice, the tangential force needed for detachment of the specimen from the ice surface was determined. For this purpose the holders were removed and the specimen left frozen to the surface of the ice. The specimen was fixed to a rocker arm connected to a pendulum dynamometer (Fig. 2). When the carriage moved, the specimen was carried along in the direction of movement and pressed on the rocker arm which in turn actuated the pendulum. To the latter was attached a mirror whereby the swing of the pendulum could be optically recorded. The deviation of the pendulum was a measure of the force that had to be applied for detachment of the specimen from the glass surface, i.e., the magnitude of the shearing force. When larger specimens were being tested, the ice cylinders adhering to the specimen were sheared off as shown in Fig. 3.

TABLE 1

Liquids Employed for Surface Treatment

Liquid No.	Name	Viscosity (in centipoises)	Density d_4^{20}
1	Methylpolysiloxane	271	0.978
2	Methylpolysiloxane elastomer	—	—
3	Ethylpolysiloxane	18.66	0.952
4		48.19	0.979
5		1161.61	1.037
6		—	—
7	Butylpolysiloxane	29.17	0.908
8		80.13	0.928
9		601.99	0.966
10	Ethyloctylpolysiloxane	—	—
11		—	—
12	Isoamylpolysiloxane	100.47	0.906
13		3724.06	0.956
14	Ethylpolysiloxane for flight tests	211.09	1.001
15	Methylpolysiloxane	347.48	0.982

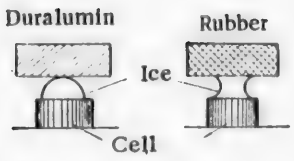

Fig. 4. Ice menisci of cells. Right: frozen to rubber; left: frozen to duralumin.

The conditions of crystallization of ice during freezing were appreciably influenced by the strength of the bond established between the ice and the surface in course of freezing. If the water in the cells is cooled gradually to the low temperature at which shearing of the ice was effected, then the shearing force was lower than when freezing on was effected directly at the low temperature.

The strength of the frozen bond increased with increasing rate of cooling presumably because a high cooling speed facilitated preliminary supercooling of the water, and its crystallization from the supercooled state was completed rapidly. Very similar conditions apply in flying when supercooled drops freeze on to the surface of the aircraft by impact. These conditions were therefore selected in these experiments.

The following experimental sequence was selected: 1) Start-up of refrigerating machine and cooling of apparatus to required experimental temperature (sample also cooled); 2) carriage put in motion and water poured into cells; 3) samples brought into contact with meniscus of water; 4) carriage moved into thermostat of refrigerator where the water in the cells was frozen at -20° for an hour.

RESULTS OF EXPERIMENTS

The principal characteristics of the liquids employed in the work are presented in Table 1. Preliminary experiments were run with specimens of rubber and duralumin. Three methods were developed for study of the influence of the polysiloxane liquids on the cohesion between ice and various surfaces of a sample:

1. A rubber specimen was immersed in the liquid or in a 15% solution thereof in carbon tetrachloride. It was then dried and heat treated at 230-235° for 5-7 min. This treatment transformed the polysiloxane into a soft elastic film with a thickness of 0.0013-0.0015 mm.

Duralumin specimens were similarly treated but the heat treatment was extended over 30 min. The following specimens (Tables 2 and 3) were so prepared: 1_1, 1_2, 2_1, 2_2, 3_1, 3_2, 4_1, 4_2, 5_1, 5_2, 6_1, 6_2, 7_1, 7_2, 8_1, 9_1, 9_2, 10_1, 10_2, 11_1, 11_2.

TABLE 2

Results of Tests of Polysiloxane Films Applied to Rubber Surface

Liquid No.	Factor by which the strength of the frozen bond was lowered in comparison with blank specimen	Method of treatment of rubber surface
1	2.3	
2	2	
3	No changes	
4	No changes	
5	1.5	
6	2	Immersion in 15% solution followed by drying in room
7	No changes	
8	No changes	
9	2.7	
10	No changes	
11	No changes	
1_1	7.6	Immersion in 15% solution, heat treatment at 200-235° for 5 min
1_2	10	Immersion in silicoorganic liquid, heat treatment at 230-235° for 5 min
1_3	10	Immersion in silicoorganic liquid
2_1	9	Immersion in 15% solution, heat treatment at 230-235° for 5 min
3_1	9.7	
4_1	6.3	
4_2	9.8	Immersion in silicoorganic liquid, heat treatment at 230-235° for 5 min
4_3	2	Immersion in silicoorganic liquid
5_1	6.1	Immersion in 15% solution, heat treatment at 230-235° for 5 min
6_1	9.2	
7_1	8	
8_1	8.2	Immersion in 15% solution, heat treatment at 230-235° for 5 min
9_1	9	
10_1	8	
11_1	6.9	

2. Liquid was applied from solution to specimens Nos. 1-11 (Table 2) without thermal treatment.

3. A film of liquid was applied to samples Nos. 1_3 and 4_3 (Table 2) by simple immersion in polysiloxane liquid without subsequent thermal treatment.

The so-prepared specimens were attached to the holders of the apparatus, brought into contact with the meniscus of the water, and the water frozen.

Results of tests on films applied to surfaces of rubber specimens with the aim of lowering the adhesion of the ice are shown in Table 2. The liquids used in the tests are correspondingly numbered in Table 1. We see from Table 2 that substances applied to rubber appreciably lower the cohesion between ice and rubber surface (by up to a factor of 10) in comparison with the blank (rubber with a clean surface). Experiments with bare duralumin specimens showed that, although in this case the surface was less easily wetted by water, the ice adhered more strongly to the surface than to a rubber surface.

TABLE 3

Results of Tests on Polysiloxane Films Applied to Duralumin Surface

Liquid No.	Factor by which the strength of of the frozen bond was lowered in comparison with bare specimen	Method of treatment of duralumin surface
1_1	2.5	Immersion in 15% solution, heat treatment at 230-235° for 30 min
2_1	4	
3_1	3.3	
4_1	2.3	
5_1	2.1	
6_1	2.4	
7_1	Nearly unchanged	
8_1	Nearly unchanged	
10_1	1.2	
11_1	2	
1_1	6	Immersion in silicoorganic liquid, heat treatment at 230-235° for 30 min
2_2	10-14	
3_2	3	
5_2	9.3	
6_2	3	
7_2	2	
9_2	2	
10_2	4	
11_2	2.6	

*Specimens 9_1 and 4_2 not tested.

In the case of the ice/rubber bond the frozen meniscus of the liquid differed in appearance from that in the case of ice/duralumin (Fig. 4).

Adhesion of ice to bare duralumin surface is so strong that very often the ice broke and the sample rebounded with a piece of ice clinging to it. Only the experiments in which the shear was clean were taken into consideration. Results of experiments with duralumin specimens are presented in Table 3. We see from this table that the most significant change in the magnitude of the shearing force is obtained on application of polysiloxane liquids Nos. 1, 2 and 5. Adhesion is lowered by a factor of 10 or more.

The results of the experiments set forth in Tables 2 and 3 showed that the first and third methods of treatment of the specimens (see above) give approximately the same effect. The second method leads to hardly any lowering of the adhesion of ice to the surface.

In the light of these results, it was decided to employ in subsequent experiments only the third method as being the simplest and having the least effect on the material whose surface was treated.

The preliminary experiments also revealed which liquids exhibited the best antiadhesive properties.

In the subsequent experiments with various polysiloxane liquids, the film was applied to the specimen by dipping. The specimen was immersed in the vessel containing the liquid and then withdrawn from the liquid at a constant rate. A change in rate led to a change in the thickness of adhering liquid. The film thickness was calculated by Deryagin's formula [6]:

$$h = \frac{k \cdot v \cdot (\eta \cdot U)^{2/3}}{V (\rho g)^{1/3} \cdot \sigma^{1/3}},$$

where k = 0.94, h = thickness of film, v = volume of dissolved substance, U = rate of withdrawal, V = volume of solution, η = viscosity of solution, ρ = density of solution, σ = surface tension, and g = the gravitational constant.

Application of the film to specimens by the dipping method was followed by tests on shearing of ice from the surface by the above procedure.

Tests results are set forth in Table 4. The best results are obtained with specimens Nos. 1, 5, 13 and 15 (Table 1). Tests repeated many times (more than 10) on a specimen coated with liquid showed that part of the liquid is "worn away" from the surface of the specimen after each repeat of the test. The liquid remains on the ice cylinder sheared away from the surface. Its film on the surface of the specimen becomes thinner and the adhesion of the ice increases.

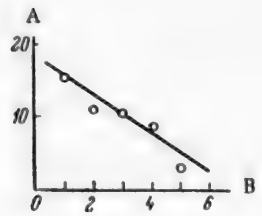

Fig. 5. Duralumin specimen coated with lacquer followed by methylpolysiloxane liquid No. 1. A) Decrease in adhesion, B) number of tests.

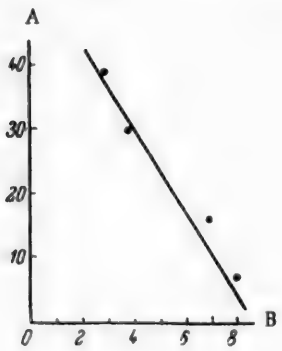

Fig. 7. Duralumin specimen coated with lacquer and then with isoamylpolysiloxane liquid No. 13. A) Decrease in adhesion, B) number of tests.

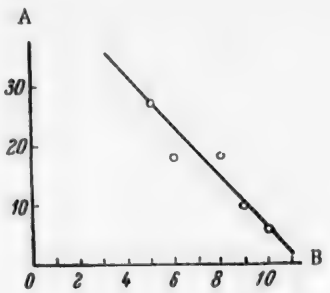

Fig. 6. Duralumin specimen coated with lacquer and then with ethylpolysiloxane liquid No. 5. A) Decrease in adhesion, B) number of tests.

In the case of the duralumin specimen coated with lacquer and then with liquid No. 1, after the fifth test the magnitude of the shearing force rose from 700 to 2883 g/cm^2. In the case of the duralumin specimen coated with lacquer and then with liquid No. 5, the shearing force rose from 100 to 400 g/cm^2, but the final value was lower than for the untreated surface. After ten tests and after it had then been wiped dry, the adhesion of ice was 6 times lower than the adhesion to the untreated specimen.

In the case of the specimen coated with liquid No. 13, 7 tests raised the shearing force from 250 to 1000 g/cm^2. Lacquer films form a good keying surface for polysiloxane liquids. The silicoorganic liquid is quickly removed from bare duralumin after 2 to 3 tests, but the liquid is retained for a longer period on lacquer-coated duralumin. The same is true of rubber and organic glass, probably due to slight swelling of the surface of the specimen.

The results obtained in repeated tests of specimens coated with liquids Nos. 1, 5 and 13 are plotted in Figs. 5 to 7. Thickness of initially applied film h = 0.1 mm. The first 2 to 3 tests of specimens coated with a thick film of liquids Nos. 5, 13 and 15 showed that ice entirely fails to stick to the surface. The adhesion is extremely insignificant on specimens coated with liquid No. 1.

On the basis of Figs. 5-7 we can conclude that the liquid on the surface is retained for a long period during repeated tests and its antisticking action persists. The thickness of the film of liquid applied to the specimen

TABLE 4

Results of Tests of Polysiloxane Films on Various Surfaces

Material of specimen	No. of liquid	Strength of adhesion for specimen (in g/cm²)		Ratio
		bare	coated	
Duralumin	1	7.600	780	10.5
Duralumin, lacquer-coated		7.600	499	15.2
Rubber		6.000	526	11.4
Window glass		8.500	1000	8.5
Organic glass (plexiglas)		4.400	508	8.6
Duralumin	3	7.600	2400	3.0
Duralumin + lacquer film		7.000	1728	4.4
Rubber		6.000	3167	1.8
Window glass		8.500	3525	2.4
Organic glass		4.400	2017	2.1
Duralumin	4	7.600	1863	4.0
Duralumin + lacquer film		7.600	1460	4.9
Rubber		6.000	1680	3.5
Window glass		8.500	2260	3.6
Organic glass		4.400	1166	8.7
Duralumin	14	7.600	860	8.7
Duralumin + lacquer film		7.600	769	9.0
Rubber		6.000	600	10
Window glass		8.500	1019	8.4
Organic glass		4.400	590	7.4
Duralumin	5	7.600	414	18.3
Duralumin + lacquer film		7.600	280	27.2
Rubber		6.000	200	30
Window glass		8.500	325	26
Organic glass		4.400	85	52
Duralumin	7	7.600	2225	3.4
Duralumin + lacquer film		7.600	1740	4.3
Rubber		6.000	900	6.6
Window glass		8.500	3250	2.6
Organic glass		4.400	2139	2.1
Duralumin	8	7.600	2000	3.6
Duralumin + lacquer film		7.600	1153	6.5
Rubber		6.000	833	7.2
Window glass		8.500	2650	3.2
Organic glass		4.400	2100	2.4
Duralumin	9	7.600	1875	4.1
Duralumin + lacquer film		7.600	692	10.8
Rubber		6.000	750	8.0
Window glass		8.500	2499	3.4
Organic glass		4.400	830	5.3
Duralumin	12	7600	1728	4.4
Duralumin + lacquer film		7600	1482	5.1
Rubber		6000	650	8.1
Window glass		8500	2861	3
Organic glass		4400	1075	4.2
Duralumin	13	7600	200	38
Duralumin + lacquer film		7500	192	39
Rubber		6000	200	30
Window glass		8500	356	23
Organic glass		4400	241	18
Duralumin	15	7600	692	12
Duralumin + lacquer film		7600	450	12
Rubber		6000	265	29
Window glass		8500	825	10.2
Organic glass		4400	400	11

TABLE 5

Dependence of the Angle of Wetting on the Liquid Applied to the Surface

Surface	Viscosity in centipoises	Angle of wetting
Untreated surface	–	86°26'
Methylpolysiloxane	271	90°
Ethylpolysiloxane	48.19	104°59'
Butylpolysiloxane	80.13	114°09'
Ethyloctylpolysiloxane	–	122°39'

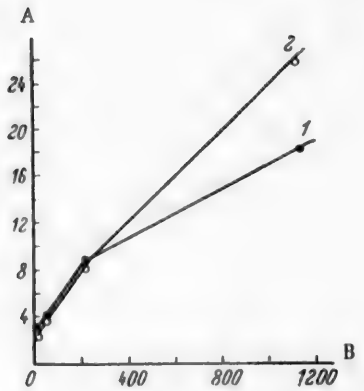

Fig. 8. Adhesivity as a function of the viscosity of the applied liquid. A) Fall in adhesivity; B) viscosity (in centipoises). Specimens: 1) aluminum, 2) window glass.

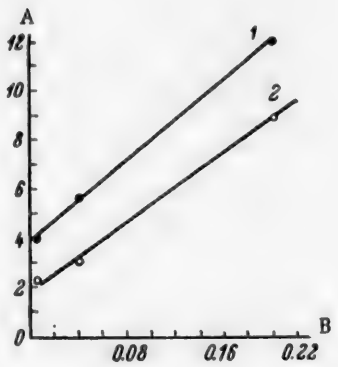

Fig. 9. Change of adhesivity of ice to surfaces with changing thickness of film of liquid No. 15 applied to a sample. A) Decrease in adhesivity, B) film thickness (in mm). Sample: 1) aluminum, 2) window glass.

plays an important part. The thicker the film, the better are its antisticking properties. The results of Table 4 show that a significant factor influencing the adhesivity of ice on surfaces is the viscosity of the liquid with which the given specimen was treated. Shearing force is plotted in Fig. 8 as a function of viscosity. This relation is an indirect expression of the dependence on the molecular weight (i.e., on the degree of polymerization). These data show that a polysiloxane liquid with a higher viscosity possesses better antisticking properties. On theoretical grounds we may infer that an important influence is exercised by the molecular weight of the organic radical, especially on the angle of wetting (Table 5).

This is not supported, however, by the data of Table 4, except in the case of isoamylpolysiloxane (No. 13); an influence of the iso structure of the organic radical can be inferred from the well-marked influence of isoamylpolysiloxane, the molecular weight of whose organic radical is intermediate between that of the radicals in butylpolysiloxane and octylpolysiloxane.

Repeated freezing of ice onto specimens with liquid coatings up to 0.1 mm in thickness led to results showing that the decreasing thickness of the liquid film with each successive test can be explained by the low internal adhesive forces in the film. This would also account for the observed lowering of the adhesivity of ice with increasing thickness of liquid film. This is also supported by the data for the influence of the thickness of the film presented in Fig. 9.

SUMMARY

1. The experimental data indicate that organopolysiloxane liquids can be employed as depressants of sticking of ice to various surfaces. The most promising of the liquidstested were methylpolysiloxanes Nos. 1 and 15, ethylpolysiloxane No. 5, isoamylpolysiloxane No. 13. These are liquids with viscosities of 300 to 1161 centipoises.

2. Liquids Nos. 5, 13 and 15 exhibit particularly good properties. They lower the shearing force by a factor of 10 when applied in a very small film thickness (h = 0.1 mm). These liquids retain their adhesion to surfaces and their films are hardly "worn away" at all after numerous refreezings of ice to the surface. After removal from the surface by careful wiping, they leave a film sufficient for lowering of the adhesion of ice by a factor of 6.

3. Especially good results are obtained on aluminum surfaces previously coated with lacquer, on rubber surfaces, and on organic glass. Less good results are obtained when ice adheres to an aluminum surface not previously coated with a lacquer film or to window glass.

4. The low viscosity of methylpolysiloxane No. 1 is a disadvantage in that the liquid easily runs down vertical surfaces.

5. The results of the present investigation justify the recommendation of organopolysiloxane coatings for surfaces liable to be exposed to ice formation since these coatings facilitate removal of ice from surfaces.

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THE POROSITY AND DISPERSITY OF THE CATALYST FOR HETEROGENEOUS SYNTHESIS OF VINYL ACETATE

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Hardly any work has hitherto been published on the influence of the dispersity of the catalyst for the vapor-phase synthesis of vinyl acetate or about the influence of the porosity of the carbon employed as catalyst support.

A complex relation between specific surface and catalytic properties has been revealed by studies of other catalytic processes which have clarified the roles of the surface and porosity of the catalysts and the influence of the degree of dispersity caused by secondary crystal formations. Conflicting conclusions have sometimes been reached by different investigators working in this field. Schmidt [1] reported proportionality between catalytic activity and specific surface. Schwab and Rudolf also reached the same conclusion [2]. These findings were not confirmed by Iozsa [3]. It was also shown that when a catalyst of given composition is used in different reactions, differing degrees of dispersity are necessary [4]. In the polymerization of acetylene an increase of surface in the catalytic zone in some cases sharply reduced the reaction velocity [5] while in other cases it had no pronounced effect [6].

Earlier work indicated a direct dependence of catalytic activity on the degree of porosity [7, 8]. Neimark [9] studied the effect of the character of the porosity of silica gel on its adsorptive and catalytic properties during hydrolysis of chlorobenzene. He established a very much more complex dependence and the existence of diffusional inhibition.

Rubinshtein [10, 11] reported a high value of dispersity caused by secondary crystal formations and the existence of an optimum of the corresponding dispersity for some reactions. He concluded [11] that the generally accepted method of low-temperature adsorption of nitrogen [12, 13] was unsuitable for evaluation of the surface of a catalyst. He recommended the introduction of the concept of the "effective porosity" which is determined by sorption of substances comparable in dimensions with the reacting molecules.

The foregoing examples show that knowledge of the influence of dispersity and porosity cannot yet be readily generalized and that more experimental data require to be accumulated in this field.

In the present work we submit the results of a study of the reaction of acetylene with acetic acid using a catalyst prepared on supports with various porosities. The catalysts were prepared by precipitation of zinc acetate on several specimens of active carbon. The total porosities and relative specific surfaces of the carbons were determined. In the first place these data could approximately characterize the magnitude of the surface per unit weight of zinc salt. It is also noteworthy that the ratio of the pore volume (ω) to the measured surface (σ) has a physical meaning and characterizes, to a certain degree, the mean radius of the pores (r). Assuming the capillaries of the carbon are cylinders, then the relation $\omega/\sigma = r/2$ is approximately valid. We can also assume that the reciprocal of r and correspondingly the surface/volume ratio will characterize the degree of "dispersity of the pores".

The size of the adsorptively active pores of carbon encompasses the region of colloidal dispersity. The experiments on formation of vinyl acetate (see below) have shown that a change in the dispersity factor of a heterogeneous catalyst within the region in question can have both a favorable and unfavorable influence on its catalytic activity.

EXPERIMENTAL

Of the several specimens of active carbon used for preparation of catalysts, granulated active carbon AG has been the most extensively studied in our earlier investigations with Ushakov and Arbuzova [14-18]. This grade of carbon was also used in the experiments to be described below. It is frequently employed for sorption and recovery of solvents. Its structure and properties have been the subject of detailed investigations [19-21]. Carbon AG belongs to the relatively finely porous type with a medium total porosity (in comparison with the majority of other carbons used by us). Alekseevskii and Vas'kovskii used the results of a study of the sorptive activity to calculate the total capillary volume and the diameters of the capillaries occupied at various concentrations. On the basis of these data the structural curve of carbon AG was constructed. The inflection point on this curve was in the region of low concentrations and, accordingly, the maximum diameter of the capillaries was in the region of 8 A. Comparison with the results of a study of similar carbons led to the conclusion that AG is characterized by the possession of two independent systems of capillaries—ultracapillaries and wider capillaries. In the further course of this paper the sample of carbon AG used as basic material is designated I. Activated carbons on an anthracite and wood basis were used for comparison: 1) similar to carbon AG but with somewhat larger pores (II and III); 2) steam-activated, decolorizing birch carbons (IV and V). Experiments were also run with finely porous bone carbon (VI). All of these carbons were treated beforehand with hydrochloric acid, thoroughly washed with water, and dried to constant weight in vacuo at a temperature of about 400°. Some of them (II and III) were subjected to supplementary activation at 850° in a carbon dioxide stream.

In special comparative experiments with catalysts prepared from ash-free and ash-containing carbon, we established that residual ash in the catalyst had no significant influence on catalytic activity.

Measurements were made, for the various samples of carbon, of specific gravity (actual, apparent and gravimetric), total porosity, sorptive capacity for several sorbates (chlorine, iodine, methylene blue); the relative specific surface was calculated. These measurements were made under the following conditions.

The true specific gravity (d) was determined with benzene in a thermostated pycnometer by the Honig method [22]. The carbon was first pulverized and passed through a 46-mesh-per-cm^2 screen. The apparent specific gravity (δ) was measured in a Tyulyukov apparatus [23] with mercury. The gravimetric density (Δ) was found by weighing a known volume of carbon. The total porosity (P) was calculated from the results of these determinations on the basis of the known volumes V_d and V_δ:

$$P = \frac{V_\delta - V_d}{V_\delta} = \frac{d - \delta}{d} .$$

The sorptive activity was found by treatment of the carbon with gaseous chlorine [24] or with 0.1 N solution of iodine in potassium iodide. The relative specific surface was found by the method of Berl and Herbert [25, 26] on the basis of sorption of methylene blue and colorimetric determination of the concentration of the solution. This method of surface determination can only give relative results applicable for comparison of similar specimens of the same or similar materials [27]. We decided that the method of Berl and Herbert might be applicable on the basis of the following additional considerations: The area occupied by the zinc acetate molecule (approx. 30 A^2), and in particular by salts of other acids that we also employed as catalysts supported on active carbon, may be considerably more comparable with the area calculated for the methylene blue molecule than, say, the nitrogen molecule (approx. 16 A^2) which is frequently used for evaluation of the surface area of various materials [12, 13]. For extremely finely porous bone carbon (VI) the dye sorption method, as was to be expected, was found inapplicable due to the phenomenon of ultraporosity. In this case the specific gravity was roughly calculated from the results of gas sorption and from data for the corresponding radii of the capillaries. A summary of the results is presented in Table 1.

Catalysts were prepared by impregnation of carbon with zinc acetate solution followed by drying at 180°. The catalytic activity was determined from the degree of conversion of acetic acid at 200° with a molar acetylene/acid ratio of 20:1. Acetylene was admitted at the rate of 10 liter/hr. The apparatus and method of regulation were the same as described previously [14-18].

Comparison of the results of this type of catalytic investigation must be made with a certain degree of caution since not only the porosity and the surface area of the catalyst can alter but also a number of other vital

TABLE 1

Characteristics of Carbon Specimens

Specimen of carbon	Sorptive activity (in g/g)		Specific gravity (in g/ml)			Porosity		Relative specific surface σ (in m^2/g)	Nominal mean pore radius $r = \frac{\omega}{\sigma} \cdot 2$ (in A)
	for chlorine	for iodine	gravimetric, Δ	apparent, δ	true, d	P (in %)	specific ω (in ml/g)		
I	0.50	0.936	0.51	0.84	1.88	55	0.66	350	40
II	0.745	0.128	0.24	0.55	1.7	68	1.23	270—280	90
III	0.58	—	0.44	0.64	1.94	67	1.03	380	54
IV	0.28	0.832	0.311	0.49	1.76	73	1.49	50	600
V	0.44	—	0.3	0.41	1.66	75	1.74	205	170
VI	0.23	—	0.69	1.3	1.8	26	0.195	~500	~8

TABLE 2

Determination of Catalytic Activity

Active carbon	Zinc acetate content (%)	Quantity of catalyst (in g)	Sorptive activity for chlorine (wt. %)	Number of moles of zinc salt per 100 A^2 (in moles per 100 A^2)	Quantity of zinc acetate in reaction space (in g)	Catalytic activity (in %)	r (in A)
V	10	14	16.0	7.25	1.5	71	600
IV	10.8	14	28	2	1.4	81	170
I	6.7	21	35	0.7	1.4	94	40
II	15	10	38	2.06	1.51	73	90
VI	12	21	1	—	2.52	15	~8

factors (such as residence time of reactants in the catalytic zone, zinc salt concentration, and rates of sorption and desorption processes).

In order that the quantity of zinc acetate participating in the reaction and the contact duration (τ) should remain roughly constant, experiments were run with various quantities of catalyst and various concentrations of zinc salt in the catalyst. For carbons I, II, IV and V the quantity of zinc salt in the reaction space was roughly constant (1.4-1.51 g), while τ was 6-7 sec. For catalyst VI the quantity of salt was somewhat larger, and τ was 4 sec. The catalyst on this carbon proved nearly inactive, differing markedly from the other carbons (under similar conditions carbon I, for example, gave a highly active catalyst). The results of this series of experiments are presented in Table 2 and Figs. 1 and 2.

Figures 1 and 2 justify the conclusion that with nearly identical residence times of reactants and quantities of zinc acetate in the reaction space, the catalytic activity is proportional to the specific surface of the support (carbon) only up to a certain limit; the increase in specific surface is associated with a decrease in the mean pore diameter; the crystals of zinc salt can then occupy a correspondingly increased number of pores from the reaction sphere. The sorptive capacity will likewise decrease (this was observed for the finely porous specimen VI). The further course of the curve in Fig. 1 cannot yet be plotted with sufficient accuracy because catalysts can be prepared with use of active carbons possessing a larger surface than specimen I and a smaller porosity than carbon VI. We may note, for example, that Berl and Burkhardt[28] succeeded in preparing (by thermal decomposition of pure hydrocarbons) active carbons with a surface of over 1000 m^2/g (as measured by methylene blue sorption). Testing of such specimens must ultimately reveal the point of inflection of the curve. Carbon VI, for which $\bar{r}$ is approximately 5 times smaller than for carbon I, is not characteristic in the present instance. Deposition of a smaller quantity of salt on this carbon VI will therefore undoubtedly give a more active catalyst than is indicated in Fig. 1 for this specimen.

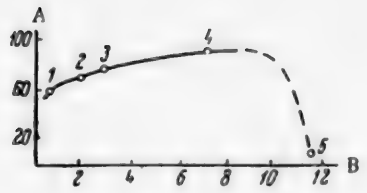

Fig. 1. Catalytic activity as a function of the surface area of the carbon. A) Conversion at 200° (in %), B) carbon surface in catalysis zone (in thousand m^2).

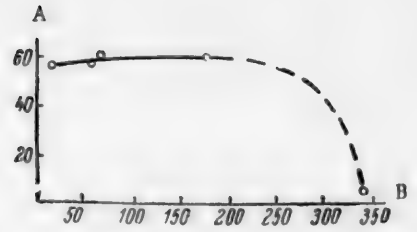

Fig. 2. Sorptive activity of catalyst as a function of the original surface area of the carbon. A) Static activity for chlorine (in % of original activity of the carbon), B) surface (in thousand m^2 per liter of catalyst).

TABLE 3

Influence of Change of Nominal Mean Pore Radius of Support

Specimen No.	Sorption activity for chlorine (%)	Specific surface (in m^2/g	Porosity		Nominal mean pore radius $\bar{r}$ (in A)	Catalytic activity (%)
			(in %)	specific ω (in ml/g		
I	50	350	55	0.69	40	99
II	60	270	68	1.23	91	58
III	58	380	67	1.063	55	99

In the experiments summarized in Table 3, carbon III was utilized. Its mean pore radius and specific surface are somewhat higher than the values for specimen I. The catalytic activity was determined with reference to the formation of vinyl acetate at 200°; τ was about 3.5 sec. The catalysts contained 12-13% zinc acetate.

The data of Table 3 show that with relatively similar values of specific surface a slight increase in mean pore radius (from 40 to 55 A) did not lead to lowering of catalytic activity.

Carbon III, used later for preparation of a zinc benzoate catalyst, was compared with carbon I in the reaction of benzoic acid with acetylene under the conditions previously specified [16]. The temperature in the middle of the catalyst bed was 290° and the duration of contact was about 3.5 sec. Results of these experiments (Table 4) show that the catalyst on carbon III was more active than the catalyst on carbon I.

Comparison of the data plotted in Figs. 1 and 2 enables us to conclude that the pore radius of the support influences the size of the zinc acetate crystals. In the case of carbon IV (containing about 10% zinc acetate), the area occupied by this salt, if in monomolecular arrangement with maximum density, would be about 2.2 times higher than the surface of the carbon. Consequently the zinc salt is not in monomolecular arrangement in this case. Nearly identical sorptive capacities for chlorine were obtained when nearly identical quantities of zinc acetate (0.191-0.196 M/liter). were deposited on carbons with various surface areas (15×10^3 to 176×10^3 m^2/liter carbon) (Fig. 2). If the crystals (the same weight in each case) distributed over carbons with various surface areas had been of the same dimensions, then the proportion of the surface occupied by them would have been larger in the case of carbon IV than in the case of carbon I or carbon V. The decrease in sorptive activity after deposition of salt should be inversely proportional to the surface of the carbon and should be expressed by a higher value in the case of carbon IV. The sorptive capacity of the catalysts (A) should be in the order $A_{IV} < A_V < A_I$, (the subscripts denote the respective specimens of carbon). Fig. 2 shows, however, that this is not the case. It would probably be more accurate to say that the size of the crystals was in the reverse sequence:
Consequently, in the larger pores the conditions of formation of crystals are such that in isolated sites they grow to a large size, instead of the given quantity of salt becoming uniformly distributed over the whole of the internal surface of the carbon. The remaining free surface of the sorbent determines the sorptive capacity.

TABLE 4

Catalytic Activity in Formation of Vinyl Benzoate

Active carbon			Catalyst		Yield of vinyl benzoate (in % of the benzoic acid)	
specimen	σ (in m^2/g)	P (in %)	amount of vinyl benzoate (%)	sorption activity for chlorine (%)	passed in	reacted
I	350	55	17.8	30	59	70
III	380	67	18	34	90	92

Hence the influence of pore size (the degree of dispersity of the pores) is extremely large since it governs the specific surface, the size of the crystals of deposited salt and the residual sorptively active portion of the carbon surface (after salt deposition). Increase in the dispersity of the pores of the carbon at first has a favorable effect on catalytic activity but an unfavorable effect is developed with further increase in dispersity. In the light of the results obtained, the most suitable pores for deposition of salt will have a region of dispersity approximating to molecular dimensions. In the case, for example, of carbon AG, over 60% of the pores have capillary diameters of less than 20 A [19]. Moreover, in agreement with current concepts [10] crystals with sizes of less than 15-20 A are unstable and can only be regarded as nuclei. We can therefore put forward the hypothesis of an interconnection between crystal nuclei and their catalytic activity in the reaction under consideration. A special set of experiments also demonstrated the high activity of catalyst which had been heated to a temperature very much higher than the melting point of the salt, say 300°.

SUMMARY

Investigation of the activity of the catalyst for the heterogeneous synthesis of vinyl acetate revealed that increase in the relative specific surface and the mean dispersity of the carbon pores increases the catalytic activity only up to a certain limit; employment of carbons with extremely small pores leads to exclusion of a considerable proportion of the pores from the sphere of reaction. Increase in pore size lowers the degree of dispersity of the salt precipitated on the carbon and correspondingly reduces the reaction velocity.

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THE COPOLYCONDENSATION OF PHENOXYACETIC ACID AND ANISOLE WITH FORMALDEHYDE

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We showed earlier [1] that although phenoxyacetic acid $C_6H_5OCH_2COOH$ does not contain phenolic hydroxyls, it enters with relative facility into a polycondensation reaction with formaldehyde in an acid medium. Soluble linear polymers of the novolak type are formed if an excess of phenoxyacetic acid is used:

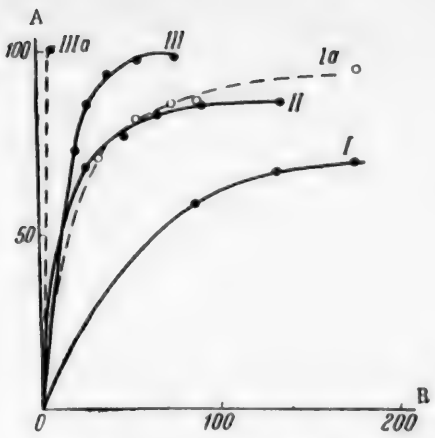
$$H[C_6H_3(OR)CH_2]_nC_6H_4OR, \text{ where } R = -CH_2COOH,$$

whereas with an excess of aldehyde infusible and insoluble cross-linked polymers of the resite type are formed. The insoluble polymers are actually modified resites since the aromatic nuclei contain $-OCH_2COOH$ groups in place of phenolic hydroxyls. These insoluble cross-linked polycarboxylic acids swell relatively slightly in water and to a very much greater extent in aqueous alkalies (due to salt formation) and enter into ion-exchange reaction with salts of metals and organic bases.

They are consequently typical weak-acid, ion-exchange resins (KFU); their exchange capacity for metal ions (5.8 mg-equiv./g) is approximately half of that of cationites of the type of cross-linked polymers of methacrylic acid.

Bresler and Samsonov [2] showed that KFU resin is considerably superior to methacrylic resins in selective absorbability of ions of streptomycin in presence of metal ions. This was attributed to the distance between the carboxyl groups being much larger than in polymers of methacrylic acid. It was therefore of interest to prepare cationites with even greater capacity for metal ions by introduction into the polymer chains of segments not containing ionogenic groups, for example methyleneanisole groups $-C_6H_3(OCH_3)CH_2-$. It appeared likely that this could be effected by copolycondensation of formaldehyde with phenoxyacetic acid and anisole. The literature does not contain any information about polycondensation of anisole with formaldehyde. We therefore decided in the first place to establish to what extent anisole is capable of entering into a reaction of this type. It was then found that in aqueous solutions formaldehyde reacts in an acid media with much greater difficulty with anisole than with phenoxyacetic acid and forms only liquid condensation products. On conducting the reaction at 100-105° in an anhydrous medium, using formaldehyde in the form of paraformaldehyde and sulfuric acid as catalyst, anisole can be brought into polycondensation reaction, although even under these conditions its reaction with formaldehyde is very much slower than that of phenoxyacetic acid. This is clearly seen from the diagram which shows the change in the free formaldehyde content of the mixture in course of its condensation with an equimolar quantity of anisole, phenoxyacetic acid or their mixture (1 : 1) in presence of 0.1 and 2.5% sulfuric acid.

In experiments with 0.1% H_2SO_4 anisole combined with only 50% formaldehyde after 75 minutes, an equimolar mixture of anisole and phenoxyacetic acid combined with 65%, and phenoxyacetic acid combined with 96%. In presence of 2.5% H_2SO_4 the formaldehyde combined with phenoxyacetic acid completely after only 5 minutes and with anisole to the extent of 82% after 130 minutes.



Rate of polycondensation of anisole (I), phenoxyacetic acid (III) and their 1 : 1 mixture (II) with formaldehyde in presence of 0.1% (I, II, III) and 2.5% (Ia, IIIa) H_2SO_4. A) Quantity of CH_2O combined (in %), B) duration in min.

In the case of copolycondensation of paraformaldehyde, phenoxyacetic acid and anisole under the same conditions, the formaldehyde was fully combined after 50-75 minutes even with a large excess of anisole and its mixture with phenoxyacetic acid. Consequently anisole reacts faster with formaldehyde in presence of phenoxyacetic acid than in its absence. Soluble products of polycondensation were only formed if the reaction mixture contained not more than one mole of formaldehyde per mole of phenolic component (Table 1).

It was desired to obtain soluble products of polycondensation of anisole, phenoxyacetic acid and formaldehyde containing groupings of anisole as well as phenoxyacetic acid in the chain. For this purpose we performed experiments in which the initial molar ratio of phenoxyacid to anisole was varied from 1 : 1 to 1 : 2 and 1 : 3. Each mixture was reacted with an equimolar amount of formaldehyde in the form of paraformaldehyde.

Condensation was performed at 100-105° in presence of 2.5% H_2SO_4 until nearly complete reaction of the components of the mixture. The residues of monomers were then distilled off with steam, and the catalyst and phenoxyacetic acid were carefully washed out of the resin with water.

We see from Table 1 that the resin yield reached or exceeded 90% of that theoretically calculated. The duration of condensation increased with progressive partial or complete replacement of phenoxyacetic acid in the initial mixture by anisole from 5 min to 5 hr, while the melting point of the condensation products gradually fell (from 130-135° to 39-48°).

All of these products were colorless, amorphous, hard but brittle resins, easily soluble in acetone. With the exception of the anisole–formaldehyde resin, they were all completely soluble in aqueous alkali solutions.

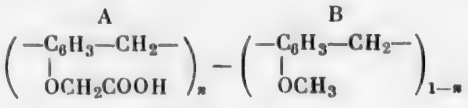
Hence the resins obtained from a mixture of anisole and phenoxyacetic acid are true polycondensates of these substances with formaldehyde and not mixtures of anisole-formaldehyde resins with carboxyanisole-formaldehyde resins.

TABLE 1

Composition and Properties of Soluble Resins Obtained with Various Ratios of Anisole to Phenoxyacetic Acid (FK)

Quantity of reactants in original mixture (in moles per mole of CH_2O)		Duration of reaction (in min)	Yield of resin (in % of theory)	Melting point (°C)	Content (in %)						Molecular weight found	Degree of polymerization n
					COOH		C		H			
FK	anisole				found	calculated	found	calculated	found	calculated		
1	0	5	95	130—135	27.0	27.7	65.5	65.4	5.3	4.9	—	—
1/2	1/2	50	95	101—111	16.2	17.0	71.2	71.4	5.8	5.7	998	6.1
1/3	2/3	75	96	88—89	10.8	11.2	74.4	74.6	6.1	6.0	615	3.7
1/4	3/4	—	—	54—56	7.7	8.5	75.3	74.5	6.4	6.2	622	3.8
0	1	300	88	39—48	—	—	78.7	79.2	6.0	6.7	663	4.6

The elemental composition of the resins and their content of carboxyl groups (found by titration) were found to be close to those calculated on the basis of the initial ratio of reactants in the reaction mixtures and the composition.



where n = 1, ½, ⅓, ¼ and 0.

The molecular weights of the resins were determined by the cryoscopic method in phenol and varied between 600 and 1000.

The molecular weights of groupings A and B in the polymer were 164 and 120 respectively; the soluble resins that we prepared therefore contained an average of 5-7 aromatic nuclei per chain. Apparently they have a structure similar to that established for formaldehydic novolaks prepared under similar conditions, namely:

$$H[C_6H_3(OR)CH_2]_nC_6H_4OR,$$

in which the OR groups of different links of one and the same chain can be OCH_3 and OCH_2COOH groups present in the polymers in the above-mentioned ratios.

The question arises as to whether the different units in the polymer chain are distributed uniformly or whether, due to the greater activity of phenoxyacetic acid, the acid is the first to enter into reaction and the anisole second. Before this can be answered it is necessary to establish whether anisole is capable of entering into reaction with formaldehyde in presence of phenoxyacetic acid when the latter (present in the mixture in excess in relation to the aldehyde) is able to bind the aldehyde completely.

Under these conditions we should expect the formation of three products: methylene-bis-phenoxyacetic acid (I), methoxybenzyl-phenoxyacetic acid (II) and dianisylmethane (III):

$$CH_2(C_6H_4OCH_2COOH)_2, \quad (I)$$

$$CH_3OC_6H_4CH_2C_6H_4OCH_2COOH, \quad (II)$$

$$CH_2(C_6H_4OCH_3)_2, \quad (III)$$

if both of the phenolic derivatives (phenoxyacetic acid and anisole) entered simultaneously into reaction with formaldehyde.

We therefore carried out joint condensation of an equimolar mixture of anisole and phenoxyacetic acid with paraformaldehyde in quantity amounting to only 0.1 of that necessary for complete binding of the above phenolic derivatives. These conditions would favor formation of the condensation products with the lowest molecular weight—diarylmethanes.

The reaction was carried out in presence of 2.5% H_2SO_4 at a temperature of 100-105° for 3 hours. The unreacted anisole was then distilled off with steam and the residual oil was treated with excess of 1 N NaOH solution for removal of acidic reaction products and catalyst. A neutral oily product was thus obtained; vacuum distillation enabled isolation (in quantity of 6.5 g) of a crystalline fraction with b.p. 172° at 3 mm Hg. Its elemental composition corresponded to dianisylmethane $(C_4H_4OCH_3)_2CH_2$.

Found %: C 78.75, H 7.21

$C_{15}H_{16}O_2$. Calculated %: C 78.95, H 7.02

TABLE 2

Exchange Capacity and Swelling of Resins in Dependence on the Anisole/Phenoxyacetic Acid Ratio in the Starting Mixture

Anisole/phenoxyacetic acid ratio in starting mixture	Moles CH_2O per phenolic nucleus taken for curing	Coefficient of swelling of the Na form in water	Exchange capacity (in mg-equiv./g)		COOH content (in %)	
			found	calculated	found	calculated
1.0	0.9	2.5	3.3	3.5	14.9	15.6
2.0	1.2	1.8	2.6	2.8	11.7	12.6
3.0	1.5	1.3	1.9	1.9	8.5	8.5

It melted at 39.41°, i.e., slightly lower than pure p,p'-dimethoxydiphenylmethane (49°).

Anisole is therefore capable of reacting with formaldehyde with formation of dianisylmethane even when a large quantity of phenoxyacetic acid is present in the reaction mixture. It is evident that already in the first step of the polycondensation there are formed, side by side with acid (I), products containing anisole residues, i.e. compounds (II) and (III). But since with further growth of the chain both of the phenolic derivatives can enter into reaction, the resultant polymers contain phenoxyacetic acid links even with excess of anisole in the original mixture. Hence the complete solubility of these products in alkali.

The above-described soluble resins can be regarded as ethers of phenol-formaldehydic novolaks in which the phenolic nuclei are linked to one another (in the o- or p-position to the ether group) by methylene bridges and which contain one active H atom at each of the central links and two active H atoms in the o- or p-position at each of the terminal links. At these positions the molecules can react with formaldehyde and become cross-linked to form three-dimensional polymers of the type of etherified resitols or resites.

As our experiments showed, this "curing" of soluble resins is actually easily realized by heating them to 120-145° in admixture with paraformaldehyde and 3% sulfuric acid (in the form of a 50% aqueous solution) until a solid and infusible resin is formed which swells in aqueous alkalies.

After pulverization, the cured resin was treated with 1 N sodium hydroxide solution for removal of soluble impurities, and then with 1 N sulfuric acid solution for transformation into the H form, and finally with water until it gave a neutral reaction. It was then dried to the air-dry state.

Both in the salt (sodium) and acid forms, the cured resins consist of hard, mechanically strong, yellow granules, insoluble in organic solvents and aqueous alkali solutions. They are weakly acid ionites (KFUA).

They swell very slightly in water when in the acid form but they increase appreciably in volume in aqueous alkalies due to transition to the salt form.

The number of carboxyl groups in the resins and their exchange capacity are easily determined by titration with 1 N sodium hydroxide solution or by back titration with alkali of the acetic acid displaced by the resins on immersion in a neutral solution of sodium acetate.

As we see from Table 2, the exchange capacity of these resins and their swelling coefficients in the sodium form vary in dependence on the anisole / phenoxyacetic acid ratio in the original mixture. An increase in the proportion of anisole from 1 to 3 moles per mole of phenoxyacetic acid in the starting mixture led to a fall in exchange capacity from 3.3 to 1.9. The latter figure is close to the capacity calculated on the assumption that the reactants entered completely into reaction with formation of a weakly cross-linked three-dimensional polymer which contains 1 to 3 moles of methyleneanisole links for each $-CH_2C_6H_3(OCH_2COOH)-$ link.

KFUA resins, containing 1 to 3 moles methyleneanisole links per methylenephenoxyacetic acid link, swelled very much less in 1 N sodium hydroxide solution than KFU resins prepared from phenoxyacetic acid alone. With increasing relative content of anisole links their coefficient of swelling fell from 2.5 to 1.3 in proportion to the content of carboxyl groups in the resins.

SUMMARY

1. It was shown that anisole in presence of traces of sulfuric acid can enter into polycondensation reactions with paraformaldehyde, with formation of low-melting anisole-formaldehyde resins, soluble in acetone but insoluble in aqueous alkalies. These resins are of the etherified phenol-formaldehyde novolak type.

2. In a reaction mixture comprising anisole, paraformaldehyde and phenoxyacetic acid, joint condensation takes place with formation of copolymers of the composition

$$[C_6H_3(OCH_3)CH_2]_n\,[C_6H_3(OCH_2COOH)CH_2]_m,$$

containing units of all of the three components in the same ratios as in the starting mixture.

3. The presence in the starting mixture of one molecule of formaldehyde per aromatic nucleus led to formation of easily fusible resins with a molecular weight of 600-1000, completely soluble in acetone and aqueous alkalies even when n/m = 3.

4. Heating of the soluble resins with paraformaldehyde in presence of sulfuric acid led to loss of solubility and conversion to cross-linked polymers of the resite type, swelling to a limited extent in aqueous alkalies and constituting weak-acid ion-exchangers (KUFA) whose exchange capacity, for an n/m ratio of 1 to 3 varies from 3.3 to 1.9 mg-equiv./g.

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ESSENTIAL OIL FROM FRUIT OF THE WILD CARROT DAUCUS CAROTA L. (CENTRAL ASIA)

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The wild carrot is widely distributed in the European part of the USSR, Central Asia, and the Caucasus. As it covers such a wide area, one would expect the appearance of various forms, some of which might be valuable agriculturally.

Our previous investigations [1] showed that the essential oils of fruit collected in different regions of our country are quite different. The constants of the oils differ considerably. The optical activity varies from α_D + 21.36° to - 44.0°; the ester number varies from 0 to 258. These data show that we can expect different compositions for the oils, depending on the habitat of Daucus carota. Having made a relatively thorough study of the oils from fruits of the carrot collected in the Caucasus [2], in the present investigation we examined the essential oils from fruits of the carrot grown in the Tashkent region (Central Asia). The essential oil had the following constants: d_4^{20} 0.9044, n_4^{21} 1.4933, α_D -23.71°, acid number 0.34, ester number 5.54 and a free hydroxyl content of 1.66%.

The oil investigated was first hydrolyzed and then fractionally distilled. The first fraction (Table 1) yielded (-)-α-pinene, whose constants and Raman spectrum corresponded to data in the literature [3]. The presence of an intense line with $\Delta\nu$ 1633 (8) cm^{-1} indicated that the pinene fraction was not homogeneous. It is possible that myrcene, which has a conjugated double bond system, was also present.

Fractions 2 and 3 (Table 1) were fractionally distilled to give a sesquiterpene fraction with b.p. 112-120° at 9 mm (Table 2), which was fractionated and repeatedly chromatographed on alkaline aluminum oxide (activity 2). Two sesquiterpenes were isolated. According to analysis and molecular refraction, the first terpene (α_D -19.93) was bicyclic with two double bonds. The presence of two double bonds was confirmed by the Raman spectrum which contained lines with frequencies characteristic of them: $\Delta\nu$ 1659 (2) cm^{-1} and 1673 (6) cm^{-1}. The latter line was very intense, indicating conjugation of the double bonds.

TABLE 1

Results of Fractionating the Essential Oil

Fraction No.	P (in mm)	Boiling Point (in °C)	Yield		n_D^{17}	α_D	OH group content (in %)
			in g	in %			
1	12	41—46	9.3	4.3	1.4700	—22.81°	0
2	10	121—125	88.7	38.56	1.4935	—33.66°	0.05
3	10	127—137	113.5	49.36	1.4970	—16.66°	3.22
4	8	137—152	7.2	3.13	1.5272	+14.25°	—

TABLE 2

Results of Distilling the Second and Third Fractions

Fraction No.	P (in mm)	Boiling Point (in °C)	Yield (in g)	n_D^{20}	α_D	OH group content (in %)
1	8	112—120	82.5	1.4920	—36.13°	0
2	9	121—123	39.0	1.4940	—35.72°	1.35
3	9	125—142	73.7	1.4990	— 6.29°	4.39
Residue	—	—	42	—	—	—

The infrared spectra of the sesquiterpene and its hydrogenation product were very similar to those of of bergamotene and bergamotane, compounds which were first described in Sorm's laboratory [4]. The hydrocarbon's constants were also close to those of bergamotene. The other sesquiterpene (α_D -66.58°), which was more difficult to elute from the chromatographic column with ligroin, was found to be the highly active β-bisabolene, a monocyclic sesquiterpene with three double bonds.

Our conclusions were supported by the following evidence: molecular refraction, addition of six H atoms, preparation of a hexachloride with m.p. 80.5-81°, formation of acetone and formic acid on ozonolysis, and spectroscopic data.

The Raman spectrum indicated the presence of double bonds: primary-tertiary and secondary-tertiary [$\Delta\nu$ 1639 (3) cm^{-1} and 1672 (7) cm^{-1}]. It should be noted that the line with the frequency $\Delta\nu$ 1672 (7) cm^{-1} was twice as intense as the line with $\Delta\nu$ 1639 (3) cm^{-1}. In addition to conjugation of the double bonds, which produces an increase in intensity, the presence of isolated double bonds with the same degree of substitution in the molecule may also produce an increase in intensity. For example, nerolidol has one primary-secondary double bond [$\Delta\nu$ 1643 (7) cm^{-1}], and two secondary-tertiary double bonds [$\Delta\nu$ 1670 (20) cm^{-1}]. The line with the frequency of 1670 cm^{-1} is considerably more intense than that with the frequency of 1643 cm^{-1}. In our case β-bisabolene has a primary-tertiary and two secondary-tertiary double bonds.

The infrared spectrum had bands with the frequencies of 1644 and 1664 cm^{-1}. The infrared spectrum was similar to the one obtained by Pliva, Herout, and Sorm [5]. The spectrum of hydrogenated bisabolene corresponded to that of bisabolane.

The high-boiling fraction (Table 2) was chromatographed on a column (aluminum oxide, activity 2) and then vacuum distilled to give an alcohol, $C_{15}H_{26}O$, which contained one double bond and was similar in properties to carotol, whose structure was determined by Sorm and his co-workers.

The Raman spectrum contained a line with $\Delta\nu$ 1670 (8) cm^{-1}, which may be assigned to a tertiary-tertiary double bond. Oxidation of carotol with $KMnO_4$ gave a triol with m.p. 142-142.5°.

On distillation of the hydrolyzed oil (Table 1), the fourth fraction yielded crystals which had m.p. 59-60° after recrystallization. The melting point, analysis, presence of three methoxyl groups, and ultraviolet absorption spectrum indicated that this product was asarone, $C_{12}H_{16}O_3$. Its picrate had m.p. 82°.

The composition of the oil, which contained (-)-α-pinene, bergamotene, bisabolene, carotol, and asarone, was closest to that of the oil from cultivated carrots (Daucus sativus L.), which was investigated by the Japanese scientists Asachina and Tsucamoto [6]. They state that the oil contained asarone, carotol, bisabolene, and daucol.

EXPERIMENTAL

Preparation of essential oil. Steam distillation of 14 kg of powdered fruits of the wild carrot yielded 269 g of essential oil (1.99%).

Fractional distillation. Hydrolysis of 250 g of the essential oil yielded 230 g of essential oil which was fractionally distilled (Table 1).

Isolation of α-pinene. Redistillation of the first fraction yielded 4 g of a substance with b.p. 37-38° (18 mm). It had the following constants: d_4^{20} 0.8516, n_D^{20} 1.4685, α_D −23.20°, b.p. 156-158° (760 mm).

Raman spectrum, $\Delta\nu$: 205 (3), 259(5), 305(2), 329(2), 360(1), 386(3), 421(2), 471-474(3), 563(4), 615(3), 640(1), 664(10), 765(4), 818(1), 840(6), 884(2), 905(3), 929(3), 951(5), 989(1), 1012(2), 1043(4), 1058(2), 1081(4), 1123(2), 1145(1), 1161(3), 1220(3), 1257(2), 1284-1306(3), 1329(4), 1375(3), 1429(8)-1449(6), 1633(8), 1659(6), 2783(10), 2872(3), 2908-2935(7), 2986(3).

Isolation of sesquiterpenes. 202 g of fractions No. 2 and 3 (Table 1) were distilled at 9 mm (Table 2).

The first fraction (112-120°) was vacuum distilled. Repeated chromatographing of the fractions obtained yielded two sesquiterpenes—bergamotene and bisabolene.

Bergamotene. B p. 96-98° (3 mm), α_D -19.93°, n_D^{20} 1.4895, d_4^{20} 0.8845 (literature data [7]).

Found %: C 87.94, 87.79; H 11.85, 11.98

$C_{15}H_{24}$. Calculated %: C 88.14, H 11.86

Raman spectrum of bergamotene, $\Delta\nu$: 625(1), 679(3), 798(1), 838(3), 1040(2), 1066(3), 1211(1), 1261(2), 1301(2), 1341(3), 1377(4), 1430-1456(8), 1659(2), 1673(6), 2828(0.5), 2930(2), 3047(4), 3128(2).

Infrared absorption spectrum of bergamotene, ν: 1653 (av),1642 (on shoulder), 1577(w), 1554(av), 1448(s), 1379(s), 1335(av), 1316(w), 1290(w), 1231(av), 1216(av), 1200(av), 1168(av), 1153(w), 1123(s), 1102(s), 1085(s), 1064(av), 1014(vs), 985(vs), 955 (vs), 927(s), 884(s), 830(s), 788(s), 769(av), 737(av).

Tetrahydrobergamotene. Bergamotene was hydrogenated in glacial acetic acid in the presence of platinum black. The hydrogenation product had the following constants: d_4^{20} 0.8639, n_D^{20} 1.4886, α_D -2.8°.

Found %: C 86.88, H 13.28; MR_D 67.10

$C_{15}H_{28}$. Calculated %: C 86.45, H 13.54; MR_D 67.05

Infrared spectrum of tetrahydrobergamotene, ν: 1471(vs), 1383(vs), 1355(vs), 1320(s), 1265(s), 1231(s), 1215(s), 1170(s), 1156(s), 1144(s), 1076(av), 1050(av), 1024(s), 999(s), 989(s), 936(av), 917(av), 891(s), 872(s), 835(s).

β-Bisabolene was more difficult to elute from the chromatography column with ligroin than bergamotene. B.p. 129-130° (9 mm), d_4^{20} 0.8689, n_D^{20} 1.4910, α_D -66.58°; it formed a trihydrochloride with m.p. 80.5-81°.

Found %: C 87.90, 87.80; H 11.85, 11.77; MR_D 68.10; M 200.9, 207.8.

$C_{15}H_{24}$. Calculated %: C 88.14, H 11.86, MR_D 67.87; M 204

Raman spectrum of β-bisabolene, $\Delta\nu$: 429(1), 452(1), 496-526(1), 700(1), 757(5), 796-844(3-1), 883-925 (2-1), 950-979(1), 1002-1026(2), 1066-1081(4), 1095-1111(4),1138-1162(5), 1194-1247(2-1), 1278-1339(2), 1378(4), 1427-1456(6), 1577(1), 1638(3), 1672(7), 2785(7), 2829-2929(3), 2971(1).

Infrared spectrum of β-bisabolene, ν: 1780(w), 1664(on shoulder), 1644(vs), 1448(vs), 1379 (vs), 1336(vs), 1312(av), 1284(av), 1239(av), 1225-1232(s), 1197(s), 1151(vs), 1108(s), 1069(av), 1046(vs), 1012(vs), 985(vs), 956(s), 916(vs), 889(vs), 861(w), 830(vs), 800(vs), 761(s).

Hexahydrobisabolene. This compound was obtained by hydrogenation of β-bisabolene in the presence platinum black in glacial acetic acid. B.p. 103-105° (5mm), d_4^{20} 0.8230, n_D^{20} 1.4530, α_D -0.43° (literature data [5]).

Found %: C 86.22, 86.26; H 14.69, 14.75; MR_D 69.11

$C_{15}H_{30}$. Calculated %: C 85.62, H 14.37; MR_D 69.27.

Infrared absorption spectrum of hexahydrobisabolene, ν: 1471(vs), 1388(vs), 1312(av), 1283(w), 1258(av), 1228(av), 1206(av), 1171(vs), 1125(av), 1098(s), 1080(on shoulder), 1057(av), 1032(av), 978(vs), 968(vs), 952(s), 933(av), 918(s), 888(s), 879(on shoulder), 855(av), 836(w).

Ozonization of β-bisabolene. Ozonolysis gave the following results: acetone 0.85 mole, formic acid 0.94 mole, and formaldehyde 0.48 mole.

Carotol. Chromatography of the higher fractions (Table 2) on aluminum oxide (alkaline, activity 2) yielded the alcohol carotol. Its constants were as follows: b.p. 117-117.5 (3 mm), α_D + 32.02°, n_D^{20} 1.4964, d_4^{20} 0.9604. OH group content 7.58% (calculated 7.65). Oxidation with $KMnO_4$ yielded a triol with m.p. 142-142.5°.

Found %: C 81.50, 81.57; H 11.84, 11.75; M 217.1, 222.7; MR_D 67.63.

$C_{15}H_{26}$. Calculated %: C 81.06, H 11.78; M 222.23; MR_D 68.13.

Raman spectrum of carotol, $\Delta\nu$: 290(1), 305(1), 336-366(1), 415-438(2), 452(1), 481(1), 509(1), 542(2), 581(2), 613(3), 653-710(2), 811(5), 842(4), 889(3), 927-1032(3), 1083-1196(8), 1374(5), 1427-1465(3), 1670(8).

Asarone. On standing, fraction No. 4 (α_D + 14.25°) deposited crystals which had m.p. 59-60° after recrystallization from hot aqueous alcohol. It formed a picrate with m.p. 82°.

Found %: C 69.46, 69.29; H 8.23, 8.24; OCH_3 2.79, 2.92

$C_{12}H_{16}O_3$. Calculated %: C 69.10, H 7.74; OCH_3 3.

SUMMARY

The essential oil from the fruit of the wild carrot (Daucus carota L.), growing in Central Asia (Tashkent Region), contains (-)-α-pinene, myrcene (?), sesquiterpenes, bergamotene (α_D -19.3°) and β-bisabolene (α_D -66.58°), the alcohol carotol (α_D + 32.02°), and asarone. The Raman spectra of bergamotene, β-bisabolene, and carotol were plotted.

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ARABOGALACTAN AND OTHER WATER-EXTRACTABLE SUBSTANCES FROM SIBERIAN LARCH

I. P. Tsvetaeva and A. V. Mercur'eva

It was previously shown [1] that there is a need for practical use of the arabogalactan of Daur larch* in the treatment of the cellulose of this important species of Eastern Siberia. Investigations [2] showed the advantage of a preliminary extraction of arabolactan with hot water from the wood chips under pressure with subsequent hydrolysis and fermentation of the galactose to alcohol. These investigations showed the importance of studying the composition of the hydrolyzates. Bearing in mind this application scheme and the fact that an average of about 10% of arabogalactan is contained in the wood of Daur larch (largely in the heart wood and only 0.6-1.4% in the sapwood), we considered that it was of practical interest to study the properties of the arabogalactan of Siberian Larch, which is also an extremely abundant indigenous species. The present work was therefore devoted to the problem.

Both of these varieties of larch—Daur and Siberian—are very similar in properties and arabogalactan content.

Despite the fact that a whole series of works have been devoted to the investigation of arabogalactan of larch, problems of the structure, homogeneity, and molecular weight of this polysaccharide remain unsolved at present [1, 3]. However, on the basis of data from recent work [4-6], it is considered that the basis of arabogalactan consists of β-D-galactopyranose residues, linked through the 1-3' positions, with most of these having side chains, consisting of β-D-galactopyranose residues, attached through the 1-6' positions. To this basis are attached arabinose, galactose, and also disaccharides of these sugars. The molar ratio of galactose to arabinose is approximately 6:1.

As investigations of the arabogalactan of Daur Larch showed [1], the substances extracted with water from the heart wood differed sharply from those extracted from sapwood. The hydrolysis products of the water-extractable substances from the heart wood were galactose and arabinose, apparently indicating the presence of arabogalactan as such. The hydrolyzates of the water-extractable substances from the sapwood consisted of glucose, galactose, mannose, arabinose, and xylose and the problem of whether the galactose and arabinose in them form an arabogalactan molecule or whether they are constituents of other hemicelluloses remains unsolved as yet. The composition of the hydrolyzates of the water-extractable substances from the heart wood was found to be more or less constant (with slight variations), while the composition of the hydrolyzates of the water-extractable substances from the sapwood was quite different for different samples. The molar ratio of galactose to arabinose in the hydrolysis products of arabogalactan from the heart wood of Daur Larch varied from 4.07 to 5.53.

In the present work we were interested in the composition of the polysaccharides extracted by water from the heart wood and sapwood of Siberian Larch.

EXPERIMENTAL

Wood samples from 20-year old Siberian Larches for the investigation were collected in the autumn of 1957 and the spring of 1958 in the nursery of the S. M. Korov Leningrad Wood Technology Academy. The trees from which the samples were collected grew very close to each other and the main difference between them was that one of them grew in a shady place and the other two had good illumination. For a light-loving species such as larch, the illumination is of great importance. Therefore, in the analysis of the samples we considered this factor.

*The term "daurskaya listvennitsa" is used in this article. The only reference I can find to this tree is in the title of of a paper, mentioned in the present article and translated in "Current Chemical Papers", where it is given as "Daur Birch". This seems an odd translation when the authors of the present article specifically state that the tree is a larch. I have therefore used the term "Daur Larch".—Translator's note.

TABLE 1

Characteristics of Wood Samples of Siberian Larch

Sample No.	No. of annual rings		Over-all diameter in bark at a height of 1.3 m (in mm)	Illumination conditions	Content of water-extractable products (%)		Time of sample collection
	heart	sapwood			in heart	in sapwood	
1	13	7	255	Good	12.5	1.9	Autumn
2	9	9	55	Poor	8.5	1.0	Autumn
3	20		208	Good	27.1	2.5	Spring

TABLE 2

Composition of Hydrolyzates of Water-Extractable Substances from Heart Wood of Siberian Larch

Sample No.	Sugar content of hydrolyzate (in weight %)		Total sugar content of hydrolyzate (in weight %)	Composition of hydrolyzate sugars (in %)		Ratio of galactose to arabinose (in moles)
	galactose	arabinose		galactose	arabinose	
1	1.718	0.366	2.084	82.4	17.6	3.93
2	1.452	0.402	1.854	78.3	21.7	3.00
3	1.864	0.358	2.222	84.0	16.0	4.55

The wood samples were reduced to powders. The powders (particle size 0.25-1.00 mm) were first freed from resin by an alcohol-benzene extraction (by the usual method) and then extracted with water [3]. The aqueous extract was filtered and evaporated to a volume of approximately 25 ml. The substances extracted from the wood were precipitated from the extract with six times the volume of ethyl alcohol, collected by filtration and dried. The product obtained was hydrolyzed with 2.5% sulfuric acid (6 hours on a boiling water bath with a water ratio of 1:50). After the hydrolysis the filtered hydrolyzates were analyzed chromatographically.

Table 1 gives data on the samples investigated.

The composition of the water-extractable products was determined chromatographically. The sugars were separated by the method described by Emel'yanova and Batrakova [7].

Paper from the Leningrad Paper Plant No. 2, 1956 issue, was used for descending chromatograms. The solvent was ethyl acetate-pyridine-water in a ratio of 5:1:5 and the developer was aniline phthalate. The sugars on the chromatogram were determined quantitatively by potentiometric ebulliostatic titration [7]. We used 0.03 ml samples of hydrolyzate for analysis.

All the numerical data given in the present article refer to the averages of 3-5 (and sometimes 7) parallel determinations. The accuracy of our determinations was an average of ± 4-5%. With a sugar content within the range 200-600 μg in the drop examined, it rose to 1-2% and with a sugar content of 10-30 μg, it fell to 8%.

Chromatograms obtained from hydrolyzates of water-extractable substances from heart wood and sapwood of Siberian Larch differed sharply from each other. In all cases the hydrolyzates of water-extractable substances from heart wood were found to contain only two sugars: galactose and arabinose. The hydrolyzates of water-extractable substances from sapwood also contained glucose, mannose, and xylose and the amounts of all the sugars were quite different in different samples. This difference could be detected even on qualitative chromatograms. Thus, here we encountered the same phenomenon as was found in the study of Daur Larch [1].

TABLE 3

Composition of Hydrolyzates of Water-Extractable Substances from Sapwood of Siberian Larch

Sample No.	Sugar content of hydrolyzate (in wt. %)						Composition of hydrolyzate sugars (in %)					Ratio of galactose to arabinose (in moles)
	galactose	arabinose	xylose	mannose	glucose	total	galactose	arabinose	xylose	mannose	glucose	
1	1.183	0.384	0.062	Traces	None	1.629	72.6	23.6	3.8	—	—	2.60
2	0.966	0.539	0.318	0.086	None	1.909	50.5	28.1	16.7	4.5	—	1.50
3	1.734	0.390	0.093	Traces	Traces	2.217	78.2	17.6	4.2	—	—	3.75

Table 2 gives the results of determining the sugars in the hydrolyzates of water-extractable substances from the heart wood.

As the table shows, the water-extractable substances were apparently actual arabogalactan, as in the case of Daur Larch. Some variation in the amounts of the constituent sugars was also observed for Siberian Larch. The ratio of galactose to arabinose nowhere exceeded 6 and varied between 3.00 and 4.55.

It may be noted that for sample No. 2, grown under poor illumination conditions, a larger amount of arabinose was found in the arabogalactan of the heart wood. In addition, there was some decrease in the arabinose in the arabogalactan of the heart wood of the sample collected in spring, as compared with the sample collected in autumn (samples No. 1 and 3, grown under good illumination conditions). The change in the composition of the polysaccharides may be connected with seasonal changes or with the conditions of growth of the tree. It is understood that all these suppositions should be checked with a large amount of experimental material, which we do not have available as yet.

Analysis data on the hydrolysis products of water-extractable substances from sapwood of Siberian Larch are presented in Table 3. As the table shows, it is difficult to establish any regularities in the composition of the water-extractable substances of sapwood. It is true that a small number of samples was investigated, but the variations in the amounts of separate sugars were so great that it is hardly possible to talk of any constancy of composition. As in the water-extractable substances of the heart wood, the extraction products of sapwood sample No. 2 contained the largest amount of arabinose and, consequently, the smallest ratio of galactose to arabinose.

As regards determining whether or not arabogalactan is actually present in the substances extracted by water from sapwood, we have insufficient data at the present time to solve this problem.

We were interested in the problem of whether there was a change in the composition of the product precipitated by alcohol from the aqueous extract of heart wood and sapwood of Siberian Larch during reprecipitation. For this purpose the carbohydrate complexes precipitated from extracts of heart wood and sapwood samples No. 1 and 2 were reprecipitated with alcohol, hydrolyzed and analyzed chromatographically. The analysis results are given in Tables 4 and 5.

As Tables 2 and 4 show, reprecipitation of the arabogalactan of the heart wood of Siberian Larch had hardly any effect on its composition. The ratio of galactose to arabinose either did not change at all or changed very little. Under our conditions, alcohol apparently precipitated from water a product of definite composition, which again gives grounds for considering that the carbohydrate complex of the heart wood is actually arabogalactan and not a mixture of separate fragments of hemicelluloses.

The reprecipitation of water-extractable substances from sapwood gave a different picture.

The reprecipitation of these substances produced a considerable change in their composition (Tables 3 and 5). In both cases reprecipitation decreased the amount of arabinose which was apparently more difficult to precipitate with alcohol than the other sugard and remained in solution. In passing we note that in the investigation

TABLE 4

Composition of Hydrolyzates of Water-Extractable Substances (Arabogalactan) from Heart Wood of Siberian Larch after Reprecipitation

Sample No.	Sugar content of hydrolyzate (in weight %)		Total sugar content of hydrolyzate (in weight %)	Composition of hydrolyzate sugars (in %)		Ratio of galactose to arabinose (in moles)
	galactose	arabinose		galactose	arabinose	
1	1.719	0.361	2.080	82.5	17.6	3.93
2	1.636	0.398	2.034	80.5	19.5	3.45

TABLE 5

Composition of Hydrolyzates of Water-Extractable Substances from Sapwood of Siberian Larch after Reprecipitation

Sample No.	Sugar content of hydrolyzate (in wt. %)						(Composition of hydrolyzate sugars (in %)					Ratio of galactose to arabinose (in moles)
	galactose	arabinose	xylose	mannose	glucose	total	galactose	arabinose	xylose	mannose	glucose	
1	1.698	0.286	0.148	None	0.063	2.195	77.4	13.0	6.8	—	2.8	4.90
2	0.740	0.257	0.210	None	None	1.207	61.3	21.3	17.4	—	—	2.43

of the reprecipitated product from sapwood of Daur Larch, the combined filtrates from six reprecipitations contained 63.95% arabinose [1]; this confirms our data. The decrease in the arabinose content immediately affected the ratio of galactose to arabinose, which increased on reprecipitation.

This indicates that the water-extractable substances of sapwood contained a mixture of separate hemicelluloses of low molecular weight. However, we cannot exclude the possibility that they contained a certain amount of true arabogalactan. Further investigations are required to elucidate this point.

Evidently the precipitation of this mixture may proceed differently even under more or less equal conditions. In this case, apparently, the solubility of the sugars, the size of their molecules, and the absolute amount of substances are of importance. In any case, there is no doubt that the composition of the water-extractable substances from sapwood changed on reprecipitation.

SUMMARY

1. Water-extractable substances from the heart wood of Siberian Larch differ in composition from those obtained from the sapwood, as in the case of Daur Larch.

2. As in the case of Daur Larch, the water-extractable substances from the heart wood of Siberian Larch are apparently true arabogalactan, consisting of galactose (78.3-84.0%) and arabinose (16.0-21.7%). The quantitative ratio of galactose to arabinose varies from 3.00 to 4.55. Reprecipitation hardly changed the composition of the water-extractable substances from the heart wood.

3. The water-extractable substances from the sapwood of Siberian Larch give galactose, mannose, arabinose xylose, and glucose in various amounts on hydrolysis. The composition of these hydrolyzates was not constant. The ratio of galactose to arabinose varied from 1.50 to 3.75. Reprecipitation of the water-extractable substances from sapwood changed the composition of their hydrolyzates.

4. The data presented above on the composition of the water-extractable substances from heart wood and sapwood of Siberian Larch should be considered in the industrial processing (hydrolysis) of this species.

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ISOLATION OF QUINIC AND SHIKIMIC ACIDS FROM PLANTS AND THEIR DETERMINATION

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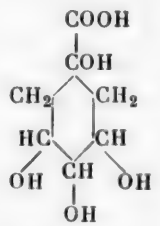
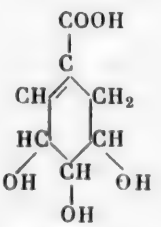
Quinic acid was isolated by Kizel' [1] from young shoots of the fir in amounts representing 10% of the weight of air-dried material. The work of Butkevish [2], Kizel', and Kursanov [3] showed that quinic acid is genetically linked with glucose and is an intermediate between carbohydrates and aromatic compounds in plant metabolism. Due to the work of Davis and his school [4, 5], attention has recently been focussed on shikimic acid as a precursor of aromatic compounds in the living cells.

Shikimic acid (3, 4, 5-trihydroxycyclohexene-1-carboxylic acid) is similar in structure to quinic acid (1, 3, 4, 5-tetrahydroxycyclohexane-1-carboxylic acid)



Quinic acid



Shikimic acid

Shikimic acid was isolated by Eijkman in 1886 from fruit of the Japanese anise Hlicium religiosum [6]. It was later detected in the leaves of Ginkgo biloba [7]. Japanese authors [8] studying the distribution of shikimic acid in plants recently isolated it from pine needles (Pinus Thunbergii Parlatore) by extraction with methanol and subsequent treatment of the evaporated extract with ethyl acetate and acetone.

Of particular interest is the work on the conversion of shikimic acid into the aromatic units of lignin (Brown and Neish [9], and Eberhardt and Schubert [10]).

When radioactive shikimic acid was introduced into sugar-cane plants, the bulk of the radioactivity was detected in lignin and its degradation product, vanillin. The distribution of the active carbon atoms in the vanillin was the same as in the shikimic acid.

We are studying the distribution of quinic and shikimic acids in plants in connection with problems of the ontogeny and phylogeny of lignin [11-12]. During the work there arose a need for the isolation of quinic and shikimic acids from plants and their quantitative determination. We isolated quinic acid from pine needles (Pinus silvestris L.), gathered in February, 1957. The quinic acid was isolated by the method of Kizel' [1], which he described for fir needles. Separation of the quinic acid from accompanying substances was difficult. The quinic acid obtained was identified by the m.p. 162°; a mixed melting point with pure quinic acid was not depressed. The purity of the preparation obtained was checked by paper chromatography when we obtained one spot with $R_f = 0.1$, which completely coincided with the R_f of the reference quinic acid. Paper No. 2 of the Volodarskii Leningrad Plant was used for chromatography. The solvent was isoamyl alcohol-formic acid-water

(100:23:77). The developer was 0.04% solution of Bromocresol Green in 96% ethanol. We isolated shikimic acid from leaves of Ginkgo biloba, gathered in spring in the Batumi botanical garden, and also from pine needles (Pinus silvestris L.), collected in February, and also from green cones of the same type, collected in June around Moscow.

Leaves of Ginkgo biloba (600 g) were cut finely and fixed with 1 liter of ethyl alcohol. The alcohol was decanted and the leaves extracted twice with alcohol for a period of 2 hours with heating on a water bath. The combined alcohol extracts were evaporated to small volume (about 100 ml) in vacuum. To the evaporated solution was added excess water to precipitate the chlorophyll. The solution was filtered and to it was added 10% lead acetate solution until precipitation was complete. The precipitate was separated by filtration through a thick layer of paper pulp and washed well with hot water. The excess lead was removed from the filtrate by the addition of 20% H_2SO_4 solution. The precipitate was removed and washed with water. The filtrate and wash waters were evaporated slightly in vacuum and further purified on activated charcoal and then on the cationite KU-2 in the H^+ form. The aqueous solution from the cationite was evaporated in vacuum to a thick sirup and the then repeatedly treated with small portions of ethyl acetate. The shikimic acid was extracted by ethyl acetate, but even after prolonged treatment much of it remained in the residue. The residue was dissolved in water. By paper chromatography it was found that the aqueous solution of the residue contained quinic and shikimic acids, while the ethyl acetate solution contained only shikimic acid. The ethyl acetate solution was evaporated and cooling the residue yielded a white precipitate of crude shikimic acid. For further purification, the preparation was repeatedly treated with acetone. The product was recrystallized from absolute alcohol. The shikimic acid preparation we obtained had m.p. 184-185°.

Found %: C 48.18, H 5.75
$C_7H_{10}O_5$. Calculated %: C 48.27, H 5.79

The preparation obtained gave a typical color reaction for shikimic acid with $NaIO_4$ and aniline. When examined by paper chromatography, an aqueous solution of the preparation gave one spot with R_f = 0.24 under the same conditions as for quinic acid.

Shikimic acid was isolated from needles and green cones of pine by the same procedure. However, freeing the shikimic acid in this material from the accompanying substances was much more difficult than in the isolation from ginkgo leaves. The shikimic acid crystallized from the mother solution very slowly.

Pure preparations of shikimic acid from pine needles and green cones had m.p. 184° and a mixed melting point with shikimic acid from ginkgo leaves was not depressed.

When examined by paper chromatography, each of these preparations gave one spot with R_f = 0.24, coinciding with the R_f of shikimic acid from ginkgo leaves. To study the distribution of quinic and shikimic acid in young parts of plants during their development and lignification, it was also necessary to have an accurate chemical method for determining them. Yoshida and Hasegawa [13] developed a chemical method for the quantitative determination of shikimic acid in plants by using the oxidation of shikimic acid with sodium periodate and subsequent condensation of the dialdehyde formed with aniline.

We used the following method for determining quinic and shikimic acids in plants.

A sample of fresh plant material (from 5 to 50 g) was pulverized and extracted twice with hot alcohol with heating on a water bath for 2 hours. The alcohol solution was evaporated to small volume in vacuum and poured into excess distilled water. The precipitate was collected and the filtrate evaporated in vacuum, diluted to a definite volume, and quantitatively (from 5 to 25 μ liters) applied to chromatography paper (paper No. 2 of the Volodarskii Leningrad Plant).

The solvent was isoamyl alcohol-formic acid-water (100:23:77). The developer was a 0.04% solution of Bromocresol Green in 96% ethanol. The positions of the quinic and shikimic acids on the undeveloped chromatograms were determined by comparison with developed chromatograms. The appropriate sections of the paper were cut out and extracted with 2 ml of distilled water for 12 hours. After the aqueous extract had been filtered, the quinic and shikimic acids were determined quantitatively in 1 ml of it.

We determined shikimic acid by the method developed by Yoshida and Hasegawa [13]. These authors observed that the product of periodate oxidation of shikimic acid reacts with aniline to give a Schiff base, which may be determined spectrophotometrically. The shikimic acid was oxidized quantitatively with periodate to aconitic dialdehyde (2-pentene-1, 5-dialdehyde-3-carboxylic acid) which was then condensed with aniline to form a bright-red color. The excess sodium periodate was destroyed by the addition of ethylene glycol.

Determination of Shikimic Acid

Periodate solution. Sodium periodate (160.5 mg) was dissolved in 25 ml of freshly prepared acetate buffer.

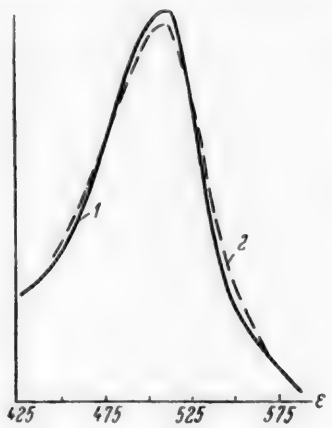
Acetate buffer. Equal volumes of 1 N acetic acid and sodium acetate solutions were mixed (pH = 4.7).

Ethylene glycol solution. Ethylene glycol (2 ml) was dissolved in 100 ml of distilled water.

Aniline solution. Distilled water was saturated with freshly distilled aniline at 25°. The aqueous layer was used. The reagent was prepared immediately before use.

Analysis procedure. To 1 ml of neutral aqueous solution, containing 40-200 μg of shikimic acid, was added 1 ml of periodate solution. The tube with the mixture was placed in a thermostat at 30° for 15 minutes, 1 ml of ethylene glycol solution added and the mixture left under the same conditions for a further 5 minutes. To the tube with the test solution was then added 1 ml of aniline solution and the mixture left at room temperature for 5 minutes. Then 5 ml of absolute alcohol was added and the solution shaken to give a clear red solution.

The pigment formed gave a sharply expressed maximum in the ultraviolet spectrum at 510 mμ. The preparation of shikimic acid we isolated was used to construct a calibration curve.



Ultraviolet absorption curves of the colored product isolated. 1) For shikimic acid; 2) for quinic acid.

The reaction was specific for shikimic acid. Sugars, amino acids, and other organic acids did not react under these conditions. The periodate reagent and a 3% alcohol solution of aniline may be used as a developer for detection of shikimic acid in paper chromatography. A red spot on a light-yellow background is obtained. This developer is more sensitive than Bromocresol Green.

We found that quinic acid also reacted with sodium periodate and its oxidation product formed a red color with aniline. The ultraviolet absorption spectrum of the colored compound was identical with that for shikimic acid (figure).

However, for quinic acid this reaction proceeded very slowly under the conditions described for shikimic acid. The reaction proceeded vigorously for quinic acid in a more acid medium, at a higher temperature, and with a higher ethylene glycol concentration.

Determination of Quinic Acid

Periodate solution. Sodium periodate (160.5 mg) was dissolved in 25 ml of 1 N acetic acid solution.

Ethylene glycol solution. Ethylene glycol (1 ml) was dissolved in 25 ml of water.

The aniline solution was prepared in the same way as for the determination of shikimic acid.

Analysis procedure. To 1 ml of an aqueous solution of quinic acid (40-200 μg of acid) was added 1 ml of periodate solution. The tube with the mixture was placed in a boiling water bath for 10 minutes. It was then cooled with a stream of water for 1 minute. To the test mixture was added 1 ml of ethylene glycol solution and the tube placed in a thermostat at 30° for 5 minutes. Then 1 ml of aniline solution was added and the mixture left at room temperature for 5 minutes. Finally, 3 ml of absolute alcohol was added, and the mixture carefully shaken and placed in the dark for 15 minutes. The red color formed was measured on an SF-4 spectrophotometer at a wavelength of 510 mμ.

Quinic and Shikimic Acid Contents of Different Tissues of Young Shoots of Pines (in milligrams per g of dry weight)

Collection date	Shoot size (in cm)	Sample	Quinic acid	Shikimic acid
June 15, 1958	35—40	Bark and needles	71.2	48.6
		Wood	3.21	6.18
		Pith	18.7	25.6
June 29, 1958	45—65	Needles	72.7	28.6
		Bark	34.6	36.7
		Cambium and precambial layer of wood	5.32	5.08
		Wood	0.52	2.2
		Top buds	15.7	12.7
July 13, 1958	40—60	Needles	88.2	37.5
		Bark	45.6	57.6
		Cambium and precambial layer of wood	3.96	3.45
		Wood	0.7	1.6
		Pith	10.67	22.5
		Top buds	11.05	20.8

A pure preparation of quinic acid was used for constructing a calibration curve. Under the conditions described, the reaction was specific for quinic acid and under these conditions, shikimic acid did not give a typical color. Sugars (glucose and xylose) and also acids (citric, cinnamic, p-hydroxybenzoic, caffeic, and chlorogenic acids) were tested under the conditions chosen for the determination of quinic acid. The reaction was negative for these substances. The methods applied to the determination of quinic and shikimic acids made it possible for us to follow the change in their content during the ontogenesis and phylogenesis of plants.

The results of these investigations have been partly published [11].

We present data we obtained on the quinic and shikimic acid contents of young shoots of pines during their development (table).

The figures presented in the table show that the greatest amount of quinic and shikimic acids are contained in the photosynthesizing tissues of the needles and green bark of young shoots. Shikimic acid predominates slightly in the bark, while quinic acid predominates strongly in the needles of the same shoots. There is a low content of the acids in the precambial zone and the wood and the amount of them falls with lignification. The pith, which consists of living cells in young shoots, contains quite a large amount of the acids, which decreases with lignification.

SUMMARY

1. Methods are described for isolating pure preparations of quinic and shikimic acids from ginkgo leaves (Ginkgo biloba) and pine needles and green cones (Pinus silvestris L.).

2. The method of Yoshida and Hasegawa was used to determine shikimic acid in the tissues of young pine shoots at various stages of lignification.

3. A method was developed for determining quinic acid on the basis of the reaction with sodium periodate and the formation of a colored compound by condensation of the oxidation product of quinic acid with aniline.

4. Data are given on the quinic and shikimic acid contents of young lignifying pine shoots.

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RAPID DETERMINATION OF ISOBUTYLENE IN PETROLEUM PROCESSING GASES

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In connection with the growth in the production of synthetic butyl rubber from isobutylene, the separation of mixtures of C_4 unsaturateds and the determination of the separate isomers is of very great importance.

Chromatographic analysis methods developed in recent years do not give sufficient resolution as yet and require further development.

Wide use is made in analysis of the sulfuric acid method of analyzing hydrocarbon gases, proposed in 1925 by Dobryanskii [1]. The theory and method of sulfuric acid analysis, into which different investigators have introduced various changes, have been given in many papers [2-14].

However, the sulfuric acid method in the form used now in the gas analysis laboratories of many research institutions cannot be used for the assay and control of gas under industrial conditions. Its main drawback is that during the great length of the analysis (one and a half hours) the analyst must all the time transfer the gas manually from the gas burette to the absorption vessel and back.

Below we present a rapid method of determining isobutylene by the sulfuric acid method.

In view of the need for reducing the laboriousness of the sulfuric acid method, we considered it advantageous to mount the gas burette and the absorber vessels on a mechanical rocker—the "apparatus for shaking tubes and flasks" put out experimentally by the construction workshops of the Academician Bogomol'ts Physiology Institute of the Academy of Sciences of the Ukrainian SSR. This apparatus made it possible to change the number of oscillations smoothly from 115 to 140 per minute. However, in the present investigation we used a step-wise change of the number of oscillations by means of an external drive, which made it possible to regulate the shaking conditions over the range of 90-240 oscillations per minute.

This obviously freed the hands of the operator from tiresome operations and accelerated the analysis itself.

Under the conditions of the sulfuric acid analysis method, the reaction of unsaturated hydrocarbons obeys the equation for a reaction of the first order:

$$K = \frac{1}{t} \ln \frac{a}{a - x}$$

Equilibrium of the reaction between gas and acid is reached more rapidly with vigorous shaking. As is known, heterogeneous reactions proceed only at the boundary surface of the phases. In our case the absorption of gas evidently occurs only in thin films of acid [4, 15]. In general, the acceleration of the interaction of gases with liquids is primarily based on the creation of hydrodynamic conditions guaranteeing a sufficient increase in the interphase surface, a decrease in diffusion resistances, and renewal of contact of the phases.

In our experiments the apparatus gave up to 240 oscillations per minute. In this case there was very vigorous mixing of the gas and acid. A voluminous foam was observed. The angle of inclination of the absorber

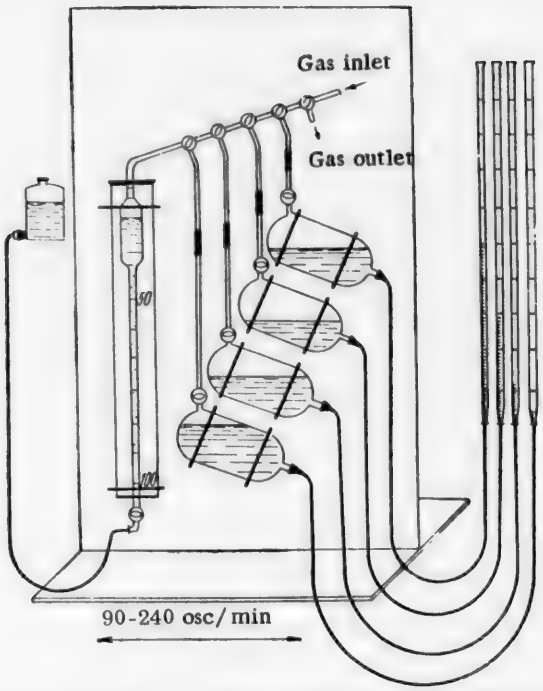

Fig. 1. Apparatus for parallel analysis of hydrocarbon gases for isobutylene.

vessel with the sulfuric acid to the horizontal, equal to ~30°, was chosen because maximum mixing was observed in this position. There was a very large interphase surface in the moving foam with rapid renewal of it and particularly vigorous mixing of the gas phase, which had a lower inertia and viscosity than the liquid.

It is noteworthy that the originator of the sulfuric acid analysis method himself did not deny the possibility of accelerating the analysis by shaking [1]. On the contrary, only the lack at that time of mechanical equipment capable of providing vigorous and uniform shaking for a long period, compelled A. F. Dobryanskii to use a manually operated apparatus for sulfuric acid analysis.

Construction of apparatus and operating procedure. The construction of the apparatus we developed for sulfuric acid analysis for isobutylene in petroleum processing gases is shown in Fig. 1. The gas burette of an Orsat apparatus and four absorption vessels, connected by a narrow-bore gas distributor were attached to a plywood panel, set in wooden stands that were firmly bolted to the upper plate of the "rocker".

The absorption vessels were connected to normal measuring burettes, filled with sulfuric acid, by means of polyethylene capillary tubes. The use of four vessels made it possible to analyze several gas samples in parallel. In addition, the apparatus could be used for analyzing gases for substances other than isobutylene.

Apart from the purely applied purposes of gas analysis, the apparatus made it possible to carry out kinetic investigations of the absorption of gases by liquids under different shaking conditions, which is of definite interest.

In gas absorption experiments we used 53 and 35% sulfuric acid. Many papers have been devoted to the choice of the sulfuric acid concentration for the analysis [3, 5, 7].

Since the volume of the reaction vessel was 200 ml* and 100 ml of gas was taken for analysis, the acid reacted with gas in a volume ratio of 1 : 1 and a molar ratio of 0.7 : 0.004, i.e., 175 times the theoretical amount of acid was used. As experiments showed, this excess made it possible to use the same acid for 8 analyses, not counting the first two experiments.

*Diameter of reaction vessel 50 mm and length 100 mm.

TABLE 1

Analysis of Hydrocarbon Gases for Isobutylene

Determination conditions	i-C_4H_8 content of gas (in %)								
	95			94		72		27	
	samples								
	1	2	3	1	2	1	2	1	2
Determination time (in min)	18	18	18	20	75	22	20	24	32
Operating conditions of apparatus (osc/min)	240	240	240	170	90	240	240	170	130
Analysis result (vol. %)	95.6	95.3	94.7	94.4	94.0	73.6	73.7	26.0	26.0
Control result of gas laboratory (vol. %)	95.0			93.5		72.5		27.0	

DISCUSSION OF RESULTS

We analyzed a number of gas samples containing various amounts of isobutylene, n-butylenes, butane, and small amounts of C_3 compounds. In most cases the analysis results for separate portions of gas samples agreed among themselves and with the data of the gas analysis laboratory with an accuracy of up to 1%. The analyses of several gases are given below (Table 1).

So that experiments on gas absorption by sulfuric acid were carried out under conditions that excluded physical solution, the acid was first saturated with gas, i.e., the first two analyses with fresh acid were ignored [13].

As the data presented show, the possibility of changing the number of oscillations of the apparatus meant that the analysis time could be shortened from 75 minutes with 90 osc/min to 25 minutes with 200-240 osc/min.

Kinetics of Interaction of Hydrocarbon Gases with Sulfuric Acid

Figure 2 shows kinetic curves of the analysis of different gases with the apparatus operating under different conditions. The curves agree well with similar data presented by other investigators [3, 16].

It can be seen that the rate of the process decreases with time, and for the final sections, the kinetics of the process do not obey the equation for monomolecular reactions. The rate constant of the process, calculated by the equation for monomolecular reactions, decreases with time. Markovich and Moor [3] explained the inconstancy of the rate by the considerable changes in the amount of gas over the time intervals recorded.

The data presented confirm (Table 2, Fig. 3) that, like a pseudomonomolecular reaction, the reaction of olefins with sulfuric acid under the conditions of sulfuric acid analysis is described by the equation for a first-order reaction.

Since this reaction is homogeneous and proceeds quite slowly under normal conditions of poor mixing, it seemed desirable to transfer it from the diffusion to the kinetic region.

To carry out the reaction under conditions excluding diffusion hindrances, we performed a series of experiments on the absorption of unsaturated hydrocarbons by sulfuric acid in the apparatus described here (Fig. 1) at high shaking speeds (Tables 1 and 2).

The graph of the relation between the reaction rate constant and the shaking speed, constructed from these data, (Fig. 4) shows a sharp demarcation between the diffusion and kinetic regions for this reaction in the apparatus described.

TABLE 2

Calculation of Rate Constants of the Reaction of Hydrocarbon Gases, Containing Various Amounts of Isobutylene, with 53% Sulfuric Acid•

$i\text{-}C_4H_8$ content of gas (in %)	95.5	94.4		93.1		30.0	
Operating conditions of apparatus (osc/min)	240	170	130	90	240	170	130
Average rate constants K	0.361	0.295	0.080	0.035	0.050	0.040	0.030

•The calculation was made by means of the equation for a pseudomonomolecular reaction: $K = \frac{2.3}{t} \lg \frac{a}{a-x}$ where x is the amount of gas that has reacted, a the initial amount of gas, K the rate constant, and t the time.

In each experiment, 100 ml of gas and 100 ml of acid were present in the vessel at the initial moment. We explain the observed transition of the reaction from the diffusion to the kinetic region by the considerable increase in the contact surface of the phases (gas-liquid) as the shaking speed of the apparatus increased. Since, according to Newton's first law, liquid and gas masses have inertia, by increasing the shaking speed, we increased the action of the absorber vessels on the contents, destroying their rest masses by moving them relatively to each other.

We should note that it is not in every case or in all systems of a similar nature that an increase in the rotation rate of the reaction vessels or the rotation rate of a stirrer leads to an actual increase in mixing, i.e., to an increase in the contact surface of the phases [17].

Thus, Davis and Shuler [4], in an experiment similar to ours on the absorption of olefins by sulfuric acid in rotating cylindrical reaction vessels, did not observe an increase in absorption when the rotation rate of their cylinders was increased.

This may be explained by the fact that in their experiments a change in the rotation rate of the reaction vessel did not lead to an increase in the boundary surface of the phases and did not eliminate diffusion hindrances as with an increase in the rotation rate, the centrifugal force pressed the sulfuric acid against the walls of the rotating cylinder in a compact layer. In addition, Bekker [18] and Davis and Crandall [19] reported a considerable increase in the absorption rate with mixing (shaking) of the system.

It should be noted that in experiments on the absorption of ethylene by sulfuric acid, a number of investigators [20-22] observed some deviations in the behavior of this gas in comparison with its homologs, propylene and butylene.

Ethylene is only absorbed by sulfuric acid with a concentration of more than 80%. An absorption maximum is observed and then the absorption rate no longer depends on the shaking speed. All this is apparently explained by the catalytic effect of intermediate products formed during the reaction.

No acceleration of the reaction of propylene and butylenes with sulphuric acid by catalysts has been reported in the literature. This difference between ethylene and its homologs should be considered in kinetic investigations of the absorption of olefins by sulfuric acid.

All that has been said above leads directly to the practical result that reactions at high rates require an apparatus providing vigorous mixing of the system. It is precisely this factor, which has usually received insufficient attention, that can lead to reactions in the true kinetic region and effect a great saving of time.

In addition, the data given in Table 2 show that the rate of gas absorption depends little on the gas composition with poor mixing of the system but is proportional to the partial pressure of the gas under conditions of high turbulence. This is in agreement with the theoretical conclusions of Kishinevskii [23] and Pozin [24].

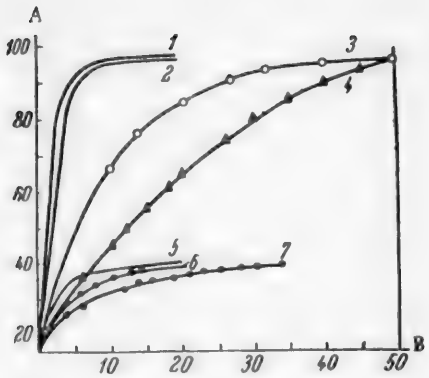

Fig. 2. Absorption of hydrocarbon gases by 53% H_2SO_4 at various shaking speeds. A) Sulfuric acid level (in ml); B) time (in min). i-C_4H_8 content (in %) and shaking speed (osc/min), respectively: 1) 95 and 240, 2) 93.5 and 170, 3) 93.5 and 130, 4) 96 and 90, 5) 26 and 240, 6) 26 and 170, 7) 26 and 130.

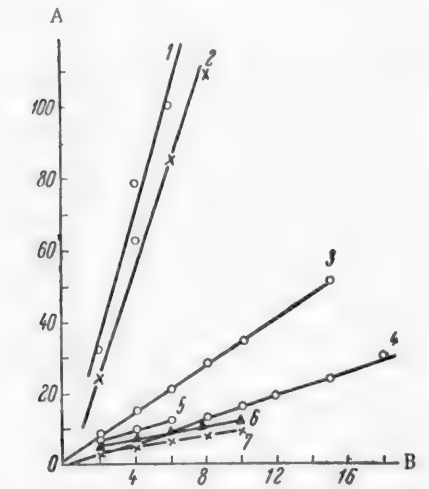

Fig. 3. Time dependence of the logarithm of the concentration $\lg \frac{a}{a-x}$ for the reaction of hydrocarbon gases with 53% H_2SO_4. A) Value of $\lg \frac{a}{a-x} \cdot 10^2$; B) time (in min). i-$C_4H_8$ content (in %) and shaking speed (osc/min), respectively: 1) 95.3 and 240, 2) 94.4 and 170, 3) 94.4 and 130, 4) 93.1 and 90, 5) 28 and 240, 6) 28 and 170, 7) 28 and 130.

With a shaking rate of 240 osc/min (high turbulence), a change in the gas composition from 95% to 30% isobutylene led to a fall in the rate of its absorption by sulfuric acid of one order, i.e., by a factor of approximately 10, while under conditions with less turbulence (130 osc/min), the rates of absorption of these gases differed by a factor of only 2.5.

In the opinion of Kishinevskii, the concentration of the chemically active component of the absorbent (in our case acid), which, to a considerable extent, determines the rate and selectivity of the reactions under poor mixing conditions, has little effect on the rate of the process under conditions of high turbulence. There is an essential difference between the kinetics of absorption processes in systems with high and low turbulence.

Experiments on the absorption of gas by dilute (35%) sulfuric acid at high shaking rates (170-240 osc/min) completely confirmed this hypothesis (Table 3).

As the table shows, the rate constants of gas absorption by dilute (35%) and more concentrated (53%) acid are similar in value.

Selectivity of the Reaction of Hydrocarbon Gases with Sulfuric Acid

As noted above, the selectivity of the reaction of sulfuric acid and hydrocarbon gases should be determined only by the acid concentration and the chemical structure of the gases and be independent of the degree of mixing of the system.

The fact is that even with extremely vigorous mixing under so-called "foam conditions" the chemical reaction between the gas absorbed and the liquid proceeds on the surface of microbubbles of gas, surrounded by thin films of liquid. These microbubbles have a high stability: as [25] ". . . at the gas-concentrated solution boundary there is orientation of complexes of solute and solvent molecules to form a quasicrystalline layer". Therefore, in this case each bubble is a separate reactor and the reaction proceeds as if under conditions without stirring, i.e., proceeds by normal molecular diffusion. In actual fact, the work of Frank-Kamenetskii [26] showed that the relative rate of motion of a gas or a liquid relative to the surface of a particle in the case of small particles and under highly turbulent conditions equals zero. The motion of the particles completely follows the turbulent pulsations. The diffusion process completely obeys diffusion laws for a stationary medium. From these arguments it follows that mixing the system only accelerates the process as a whole and does not affect the selectivity of the reaction.

To study the selectivity of gas absorption by 35 and 53% sulfuric acid we carried out experiments with a gas which did not contain isobutylene. This gas was obtained by dehydration of pure n-butyl alcohol over an aluminum oxide catalyst at 375-390°, and then the isobutylene was extracted from it with sulfuric acid. Experiments

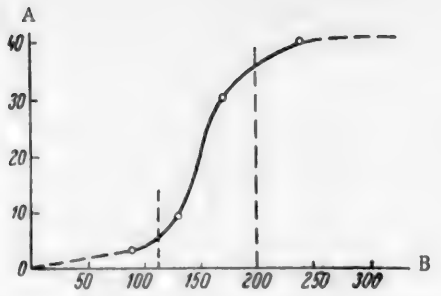

Fig. 4. Demarcation of diffusion and kinetic regions of the reaction of isobutylene with 53% H_2SO_4. A) Rate constant of reaction $K \cdot 10^2$; B) shaking conditions (osc/min).

with 62 and 93% butylene (the pure gas was diluted with air) showed that under various shaking conditions (145-250 osc/min), 35% sulfuric acid did not absorb the butylenes at all, while 53% acid absorbed them at a constant rate (0.1 ml/min). We used this value of the rate of absorption of butylenes to introduce a correction in the analysis of gases with 53% sulfuric acid under the conditions of our system.

TABLE 3

Comparison of the Absorption of Isobutylene (96-98% pure) by 35 and 53% Sulfuric Acid

Intervals between determinations (in min)	Rate constants K* at the given H_2SO_4 concentration		
	53%	53%	35%
	mixing rate (osc/min)		
	240	170	240
2	0.37	0.28	0.22
4	0.45	0.36	0.31
6	0.38	0.32	0.37
8	0.32	0.27	0.36
10	0.26	0.23	0.33
12	—	—	0.29

*See footnote to Table 2.

The experimental data obtained make it possible for us to recommend 35% sulfuric acid for analyzing hydrocarbon gases for isobutylene in the apparatus described.

SUMMARY

1. The rapid method of analyzing petroleum processing gases for isobutylene (with an accuracy of ± 1%) on a specially designed apparatus shortened the analysis time in comparison with existing procedures, calculated for one absorber vessel, by a factor of approximately 20.

2. Kinetic and diffusion regions of the reaction were demonstrated by changing the mixing.

3. It was established that there is a change in the selectivity of isobutylene absorption by acid of different concentrations under vigorous mixing.

4. The use of 35% sulfuric acid is recommended for analytical purposes instead of 53% acid, used in the manually operated apparatus for the sulfuric acid method.

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REFRACTIVE DISPERSIONS OF DEAROMATIZED PETROLEUM FRACTIONS

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Over the past 15-20 years there has been considerable expansion of methods of analysis of complex hydrocarbon mixtures by measurement of the refractive dispersion [1-8]. In the application of dispersion to analysis, use was originally made only of the specific dispersion, $\delta_{\lambda_1\lambda_2}$, which is merely the difference in the specific refractions calculated by the Gladstone-Dale formula for two wave lengths of light λ_1 and λ_2:

$$\delta_{\lambda_1\lambda_2} = \frac{n_{\lambda_1} - n_{\lambda_2}}{d} \cdot 10^4. \tag{1}$$

However, it was later shown [9] that for the determination of aromatic hydrocarbons it is more expedient to use the relative dispersion:

$$\omega_{FC} = \frac{n_F - n_C}{n_C - 1} \cdot 10^3 \tag{2}$$

or

$$\omega_{FCD} = \frac{n_F - n_C}{n_D - 1} \cdot 10^3, \tag{2a}$$

where, n_F and n_C are the refractive indices for the blue and red hydrogen lines.

In addition to the more commonly used functions (1) and (2), expressions for specific and relative dispersion derived from the well-known refraction formula of Lorenz and Lorentz $r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$: have also been proposed:

$$\delta_R = \left(\frac{n_F^2 - 1}{n_F^2 + 2} - \frac{n_C^2 - 1}{n_C^2 + 2} \right) \frac{1}{d} \cdot 10^4 \tag{3}$$

and

$$\omega_R = \left(\frac{n_F^2 - 1}{n_F^2 + 2} - \frac{n_C^2 - 1}{n_C^2 + 2} \right) \cdot \frac{10^3}{n_D - 1}. \tag{4}$$

The Lorenz-Lorentz specific dispersion (3) has been recommended in lieu of the Gladstone-Dale specific dispersion (1), and has been used in the work of the Institute of Petroleum, USSR [12], although proof that such a change in the formulas used for calculating the specific dispersion is expedient has not been published.

TABLE 1

Petroleum Samples Investigated•

Sample No.	Formation	Well No.	Ratio of naphthene to paraffin hydrocarbon content••	Age of reservoir rocks	Oil- and gas producing region
1	Klyuchevskaya ploshchad	P-1	0.195	Mesozoic	Chelyabinsk brown-coal basin
2	Osinsk	1-P	0.212	Lower Cambrian	Irkutsk amphitheater
3	Dunlyan	14	0.216	Tertiary	China
4	Romashkin	6	0.362	Devonian	Volga-Ural
5	Mukhanovo	74	0.374	Permian	
6	Upper Chysovskii rocks	1-B	0.387	Carboniferous	
7	Oisungur	40	0.442	Miocene	Tersko-Dagestan
8	Angot	2	0.452	Cretaceous	Afghanistan
9	Ozek-Suat	69	0.464		Tersko-Dagestan
10	Arlan	38	0.492•••	Carboniferous	Volga-Ural
11	October	87-17	0.507	Miocene	Tersko-Dagestan
12	Syzran'	111	0.528[15]	Carboniferous	Volga Ural
13	Mikhailov	29	0.554	Devonian	
14	Vol-Vozh	21	–	Devonian	Timan-Pechora
15	October	78-13	0.659	Miocene	Tersko-Dagestan
16	Gora-Gorskaya	214	0.736		
17	Bitkov	81	0.725[16]	Paleocene	Eastern Carpathians
18	Palvantash	59	0.820[17]	Tertiary	Fergana
19	Chuél'skoe	7-P	0.842	Cretaceous	Western Siberia
20	Glubokii Yar il. Kipyachaya	566	0.888	Paleocene	Kuban-Black Sea
21	Malgobek	68-2	0.947	Miocene	Tersko-Dagestan
22	Duzlak	32	0.998	Cretaceous	Tersko-Dagestan
23	Nebitdag	258	1.057[17]	Tertiary	Balkan region
24	Nazinskaya	–	1.09	Jurassic	Western Siberia
25	Gora-Gorskaya	244	1.29	Miocene	Tersko-Dagestan
26	Surakhan	1122	1.43[18]	Pliocene	Azerbaidzhan
27	Kaspiisk	–	–	Miocene	Tersko-Dagestan
28	Makhach-Kala	–	–		
29	Kayakent	–	–		
30	Sagiz	101	1.44	Lower Cretaceous	Ural-Emba
31	Sandy Umet	–	1.68	Carboniferous	Volga-Ural
32	Old Grozny	11-977	1.79	Miocene	Tersko-Dagestan
33	Old Grozny	19-414	–		
34	Sagiz	69	1.99	Jurassic	Ural-Emba
35	Surakhan	293	2.07[18]	Pliocene	Azerbaidzhan
36	Atashke	–	–		
37	Koschagyl	234	2.16	Jurassic	Ural-Emba
38	Dossor	–	2.26[19]		
39	Pil'tun	6	2.43	Miocene	Sakhalin
40	Chakhnaglyar	2.43	2.92[18]		Azerbaidzhan
41	Malgobek	237-4	3.48		Tersko-Dagestan
42	Bogachevka	P-2	5.14	Tertiary	Kamchatka
43	Érri	–	–	Miocene	Sakhalin
44	Sabo	–	–		

• See overleaf for notes.

TABLE 1 (Continued)

Sample No.	Formation	Well No.	Ratio of naphthene to paraffin hydrocarbon content••	Age of reservoir rocks	Oil- and gas-producing region
45	Sumatra	–	–	Neocene	Indonesia
46	Kulsari	11	7.61	Jurassic	Ural-Emba
47	Chongalek	–	189[20]	Miocene	Kuban-Black Sea

•Arranged in the order of increasing ratio of naphthene to paraffin hydrocarbon content.
••In the gasoline-kerosene fractions boiling to 300°.
•••In the 250° e.p. gasoline fraction.

The function ωR (4) has been proposed for elimination of the slight corrections for the deviation of refractive dispersion from additivity which occurs with some mixtures of aromatic hydrocarbons [13]; however, this function nevertheless exhibits significant deviations from additivity [14].

The major requirement to be satisfied by an expression for the refractive dispersion, when the dispersion is to be used for the determination of aromatic hydrocarbons, is the highest possible degree of constancy of the values of the dispersion of paraffinic and naphthenic hydrocarbons with respect to the difference in the dispersion of aromatic and saturated (!) hydrocarbons. In order further to develop analytical methods based on dispersion measurements and to increase their accuracy, it is necessary to select a dispersion function which best satisfies the indicated requirement.

To the present time, comparison of the various dispersion formulas from the point of view of the constancy of the dispersion values they yield has been made only on the basis of data on individual paraffins and naphthenes. These comparisons [1, 13] led to the conclusion that relative dispersion values calculated by means of Eq. (2) are the most nearly constant.

However, the degree of accuracy with which the average dispersion values established for individual hydrocarbons correspond to the values obtained with dearomatized petroleum fractions is still obscure, nor is it clear within what limits these values can vary. In order to increase the accuracy of dispersion methods of petroleum analysis, it appeared to be of considerable interest to compare directly the various refractive dispersion functions as applied to dearomatized petroleum fractions, to determine the corresponding average values, and to determine the deviations from them.

A definitive approach to these questions requires the investigation of petroleums which differ to the maximum extent with respect both to group composition and to individual hydrocarbon composition.

Characteristics of the Petroleums Investigated

The samples selected for this investigation, which are listed in Table 1, represent petroleums from all of the major petroleum- and gas-producing regions of the USSR. Three samples of foreign petroleum (China, Afghanistan, and Indonesia petroleums) were also investigated.

Of the 47 petroleums investigated, 15 were from platform type formations (Nos. 2-5, 10, 12, 13, 24, 30, 31 34, 37, 38, and 46), and of these, Nos. 30, 34, 37, 38, and 46 were from salt dome regions; the remaining 32 samples were from regions in which there is foothill folding, intermountain basins, and folded zones. The paleogeographical environment during the formation of the petroleum-bearing deposits were ocean, lagoon, and continental phases, during which terrigenous and carbonaceous deposits were laid down. The petroleums investigated were laid down. The petroleums investigated were contained in rocks of Paleozoic, Mesozoic, and Cenozoic ages, and in two cases (Samples Nos. 13 and 19), the oil was directly in the crystalline bed rock.

The extreme variation of these petroleums with respect to geographic location, tectonic background, and age of the reservoir—collecting—rocks ensured maximum differences with respect to the materials from which

the petroleum was formed, with respect to factors involved in the formation of the petroleum, and, consequently, with respect to chemical composition.

The group compositions of the gasoline-kerosene fractions with 300° end points are shown in Fig. 1, and were calculated mainly from data obtained by co-workers in the petroleum laboratory of the VNIGRI [All-Union Petroleum Scientific Research Institute for Geological Survey]: A. I. Bogomolov, G. M. Vasil'eva, F. B. Indenbom, A. K. Kotina, N. V. Strigaleva, and V. K. Shimanskii. The authors take this opportunity to express their appreciation to these comrades for the gift of the petroleum samples used in our work. In the case of nine of the samples, we were limited to literature data on the group composition [15-20], which gave an orientational idea of the type of petroleum sufficient for our purposes.

Data on the group compositions were obtained by the maximum-aniline-point method using GrozNII [Grozny Petroleum Scientific Research Institute] coefficients. It may be seen in Fig. 1 that we included all of the known petroleum types from paraffin base to naphthene-aromatic base.

EXPERIMENTAL

The majority of the fractions investigated were obtained by the following method: A broad fraction with an end point of 310-320° was distilled from the petroleum sample; this was twice• treated with a three-fold volume of 99% sulfuric acid for a period of half an hour, and it was then washed and dried as usual. The resulting wide-boiling, dearomatized fractions were distilled into standard 25-50° fractions using a flask fitted with a 40-centimeter Vigreux column. Some of the petroleums (in the initial stages of the work) were distilled into standard fractions prior to the sulfuric acid treatment.

Since the distillation was carried out at atmospheric pressure, certain fractions boiling in the range of 250-300° were slightly yellowish. Such fractions were treated by agitation with silica gel (approximately one tenth of the weight of the fraction) until the color disappeared.

Completeness of the removal of aromatic hydrocarbons was checked by the formalite reaction, both in the broad gasoline-kerosene fraction as a whole and in the standard 25-50° fractions. For the dispersion measurements, fractions were used which did not give even a weak-yellow color when allowed to stand for a period of half an hour.

The optical density was also determined for selected samples; the determinations were carried out at each ten mμ over the wave-length region from 240 to 330 mμ using an SF-4 spectrophotometer. The content of aromatic hydrocarbons in the dearomatized fractions did not exceed 0.1%, and as a rule it was significantly less.

The refractive indices of the fractions were measured with an IRF-23 refractometer, No. 560,091, fitted with an improved thermostating apparatus; the refractometer was checked against glass standards with known dispersions. An SNA-2 sodium lamp and a GV-3 Geissler tube served as light sources. The temperature was maintained in the limits of 20.00 ± 0.03° by means of a Bobzer Model U-8 circulating thermostat.

The densities of the dearomatized fractions were determined pycnometrically at a temperature of 20.00 ± ± 0.03°. Subsidiary tables [22] were used for the density calculations.

RESULTS OF THE INVESTIGATION AND DISCUSSION

Tables 2 presents a condensed summary of the experimental data obtained with the 243 samples of dearomatized gasoline and kerosene fractions from the 47 petroleums indicated in Table 1. Table 2 contains the maximum, minimum, and average values of all four of the refractive dispersion functions (1)-(4).

As may be seen from the data presented, the Gladstone-Dale specific dispersion calculated by Eq. (1) was the most constant for any of the dearomatized fractions. Its average value for gasoline fractions, δ_{FC}, was 97.3, which, within the limits of accuracy of the measurements, is in agreement with the average value of 97.4 recently established on the basis of the most accurate data for individual paraffins and naphthenes [2]. Moreover, it should

•Ultraviolet absorption spectra showed that a single sulfuric acid treatment was insufficient; in a number of cases, more than 0.1% aromatic hydrocarbons remained.

TABLE 2

Dispersions of Dearomatized Petroleum Fractions

Boiling range of fraction (in °C)	No. of fractions investigated	Relative dispersion						Specific dispersion						Average deviation (in %)*			
		ω_{FC}			ω_R			δ_{FC}			δ_R						
		average	minimum	maximum	average	minimum	maximum	average	minimum	maximum	average	minimum	maximum	$\Delta\omega_{FC}$	$\Delta\omega_R$	$\Delta\delta_{FC}$	$\Delta\delta_R$
60—95	15	17.34	17.31	17.60	93.3	92.2	94.7	97.2	95.9	98.3	52.5	52.0	53.6	0.5	0.5	0.6	0.9
95—122	21	17.54	17.35	17.68	93.2	92.6	94.4	97.5	97.0	98.2	52.1	51.3	53.2	0.4	0.2	0.3	0.7
122—150	31	17.59	17.45	17.77	92.6	91.8	93.0	97.5	97.8	98.1	51.6	50.7	52.3	0.5	0.3	0.3	0.5
150—175	23	17.60	17.46	17.76	92.0	91.6	92.8	97.2	96.7	98.0	51.1	50.3	52.0	0.3	0.3	0.3	0.7
175—200	25	17.64	17.46	17.75	91.7	90.1	92.4	97.1	96.1	98.0	50.8	49.3	51.7	0.3	0.4	0.4	1.0
150—200	18	17.62	17.52	17.78	92.0	91.2	92.6	97.3	96.7	98.1	51.0	49.5	51.9	0.4	0.4	0.3	0.6
200—225	23	17.66	17.49	17.83	91.4	91.0	92.0	97.1	96.4	97.8	50.5	49.6	51.1	0.4	0.2	0.4	0.9
225—250	19	17.66	17.55	17.79	91.2	90.9	91.7	97.1	96.4	97.8	50.4	49.6	51.0	0.4	0.2	0.4	1.0
200—250	25	17.69	17.58	17.86	91.5	90.4	92.5	97.1	96.2	97.9	50.5	49.4	51.6	0.3	0.4	0.4	0.8
250—275	18	17.69	17.61	17.82	91.0	90.3	92.2	97.1	96.4	98.4	50.2	49.4	51.2	0.3	0.6	0.6	1.1
275—300	9	17.68	17.63	17.81	90.4	89.8	91.4	97.0	96.2	97.6	49.8	49.3	50.3	0.2	0.4	0.4	0.6
250—300	16	17.71	17.59	17.92	91.2	90.3	92.3	97.2	96.1	98.3	50.4	49.1	50.7	0.4	0.4	0.7	0.7
60—200		17.55	17.31	17.78	92.5	90.1	94.7	97.3	95.9	98.3	51.5	49.3	53.6	0.8	0.93	0.49	1.81
200—300		17.68	17.49	17.92	91.1	89.8	92.5	97.1	96.2	98.4	50.3	49.1	51.6	—	—	—	—

*From the average value for the given fraction.

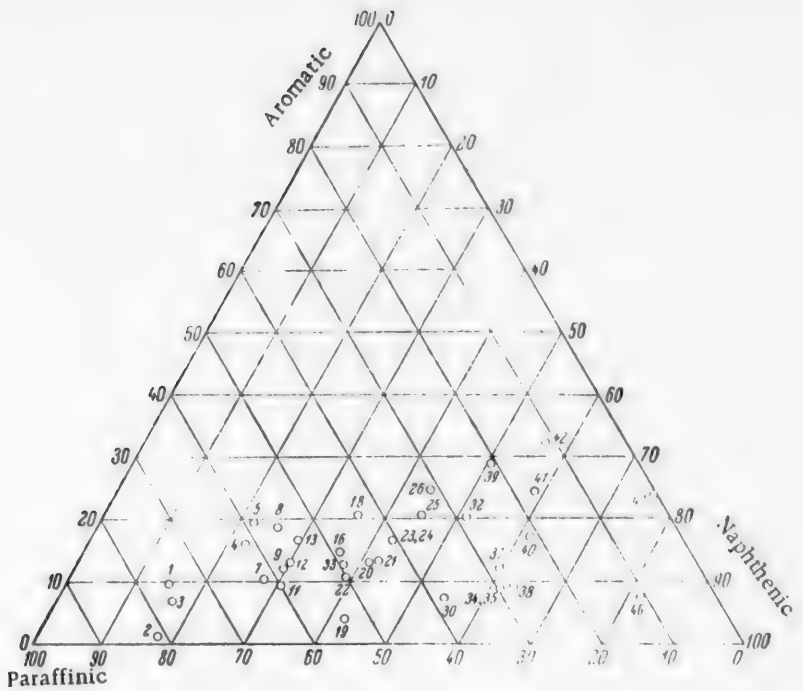

Fig. 1. Group chemical composition of the gasoline-kerosene fractions of the petroleums investigated. The numbers correspond to the sample numbers given in Table 1.

TABLE 3

Errors in the Determination of Aromatic Hydrocarbons Associated with Deviations of the Dispersion from the Over-all Average Value for Gasoline Fractions

Boiling range of fraction (in °C)	Error (in absolute %) for determinations using the values of			
	ω_{FC}	ω_R	δ_{FC}	δ_R
60—95	1.2	1.8	0.7	3.4
95—122	0.6	1.3	0.5	2.2
122—150	0.9	0.6	0.6	1.0
150—175	0.9	1.2	0.5	2.3
150—200	1.2	1.5	0.4	2.3
175—200	1.3	2.2	0.9	4.1

be noted that the average experimental value of the specific dispersion of the dearomatized petroleum fractions (97.3) differs appreciably from the δ_{FC} values of 99 or 98 used in earlier work. The use of these high values obviously led to systematically low aromatic hydrocarbon contents and, probably, was one of the reasons why the specific dispersion method proved to be less accurate than the relative dispersion method [14].

The specific dispersion calculated by the Lorenz-Lorentz formula (3) was the least constant of all of the refractive dispersion functions considered, and it gave a very significant and regular decrease in the average values with an increase in the boiling range of the fraction. The differences between the maximum and minimum values of δ_R for each of the boiling ranges was significantly greater than for the other formulas considered, and the deviation from the average value for each fraction was, on the average, 0.8%, i.e., twice as great as for the other expressions for specific dispersion. Thus, the use of the δ_R specific dispersion in analysis can lead only to a significant decrease in the accuracy of the analytical determinations, and such use can in no way be justified.

The degree of constancy of the relative dispersion ω_{FC} for gasoline and kerosene fractions was, in general, the same as for the specific dispersion δ_{FC}—the average deviation was 0.4%, and in the case of gasoline fractions, the variation in ω_{FC} values was greater than that of the δ_{FC} values, while in the case of the kerosene fractions, the reverse was true. However, in contrast to the δ_{FC} specific dispersion, the relative dispersion of the dearomatized

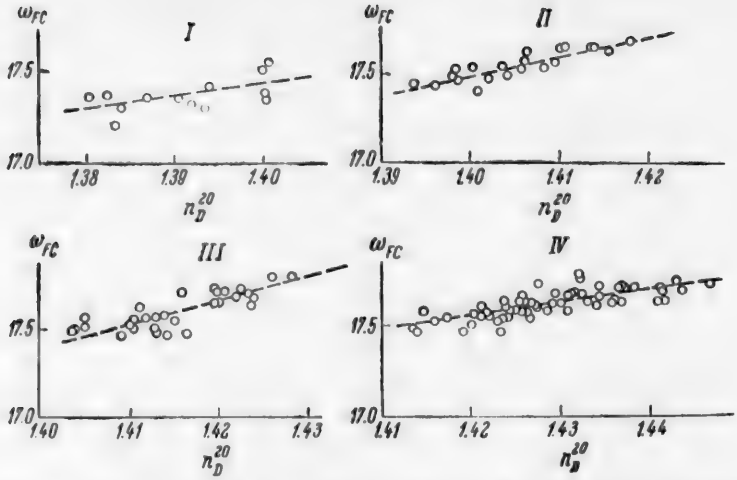

Fig. 2. Dependence of the relative dispersion of dearomatized gasoline fractions on refractive index. Boiling ranges of the fractions (in deg C): I) 60-95; II) 95-122; III) 122-150; IV) 150-200, 150-175, and 175-200.

fractions displayed a small but clear dependence on the boiling range of the light fractions. The dearomatized gasoline fractions gave appreciably lower values of specific dispersion (on the average, ω_{FC} = 17.31), than did the heavier gasoline and the kerosene fractions (ω_{FC} = 17.6-17.7). In this connection, the average value of ω_{FC}, 17.68, for the kerosene fractions was appreciably higher than for the gasoline fractions.

The function ω_R (4) had the opposite trend with an increase in the boiling range of the fractions; it decreased in a regular manner with the transition from the light to the heavier fractions, approximately by 3%. The observed change in δ_R (4.7%) was 1.5 times as great as the change in ω_R, but the latter was approximately 1.5 times as great as the change in the ω_{FC} relative dispersion with the transition from the 60-95° gasoline fraction to the 250-300° fraction (2.1%).

Thus, on comparing the expressions for refractive dispersion based on the formula of Gladstone and Dale (1, 2) with Formulas (3) and (4), including the Lorenz-Lorentz function, we see that the use of the latter function has no advantages, and leads to an appreciable deterioration of the corresponding values with respect to the requirements mentioned above for dispersion analysis.

Table 3 presents the values of the absolute errors in determinations of aromatic hydrocarbons in gasoline fractions caused by deviations from the average values for the gasoline fraction as a whole; these are the average values presented in the penultimate line of Table 2. It is not difficult to see that the best results were obtained with δ_{FC} dispersion (1), second place went to ω_{FC} (2) relative dispersion, and functions (3) and (4) gave very large errors.

The ω_{FC} relative dispersion was somewhat inferior to the δ_{FC} specific dispersion with respect to constancy of the average values for the dearomatized fractions; however, it surpassed δ_{FC} with respect to additivity as defined in reference [23], and is enormously more convenient for routine analyses, being free from the requirement of laborious density determinations.

It seemed desirable to improve further the relative dispersion method and to seek a formula which still better satisfies the requirements for dispersion analysis.

A comparison of the values of the relative dispersion of different dearomatized gasoline fractions leads to the conclusion that dearomatized fractions with the higher refractive indices as a rule have the higher relative dispersion. This dependence of the value of ω_{FC} on index of refraction is observed not only when comparing fractions with different boiling ranges but also on comparing fractions having the same boiling range but different group compositions. The latter circumstance, which is clearly illustrated in Fig. 2, is, in turn, associated with the well-known difference in the average values of the dispersion of different classes of saturated hydrocarbons [9]; dispersion increases on going from the weakly diffracting paraffins to highly refracting cyclohexane hydrocarbons.

TABLE 4

Dispersiometric Coefficients of Dearomatized Petroleum Fractions

Boiling range of fraction	Value of D_{FC}			Average deviation ΔD_{FC} (in %)	Error* in the determination of aromatic hydrocarbons (in absolute %)
	average	minimum	maximum		
60—95	193.9	192.3	195.1	0.4	0.8
95—122	194.8	193.5	195.7	0.3	0.6
122—150	194.8	193.2	196.2	0.3	0.6
150—175	194.4	193.1	195.8	0.2	0.4
175—200	194.4	192.9	195.7	0.3	0.4
150—200	194.5	193.6	196.1	0.3	0.5
200—225	194.4	193.2	195.5	0.3	—
225—250	194.3	193.5	195.4	0.3	—
200—250	194.7	193.8	196.0	0.2	—
250—275	194.2	193.5	196.0	0.2	—
275—300	194.0	193.2	195.5	0.3	—
250—300	194.6	193.5	196.4	0.3	—
60—200	194.5	192.3	196.2	0.42	—
200—300	194.4	193.2	196.4	—	—

*Due to deviations in D_{FC} from the over-all average value for gasoline fractions.

The observed "trend" in the values of ω_{FC} for mixtures of saturated hydrocarbons as a function of their index of refraction indicates that the average dispersion $n_F - n_C$ of the dearomatized fractions is, strictly speaking, proportional not to the value $n_C - 1$ (or $n_D - 1$) but to some more complex function of the index of refraction. Recalling the high degree of constancy of δ_{FC} specific dispersion of the dearomatized fractions, it would seem possible to approach the determination of the manner in which the average dispersion depends on index of refraction through the use of the relationship between the density and refractive index of hydrocarbons, the refractive difference ("refractivity intercept") r_i:

$$r_i = n - \frac{d}{2} \tag{5}$$

The refractivity intercepts of paraffins, monocyclic naphthenes, and bicyclic naphthenes boiling up to 250° are 1.046, 1.040, and 1.033, respectively [2]. For our purpose, it is quite sufficient to confine our considerations to an over-all average value r_i for saturated hydrocarbons, 1.04, disregarding the difference between n_D and n_C, which is unimportant in the present case.

Taking $r_i = 1.04$ and substituting the value of d from Eq. (5) into Eq. (1), we obtain a new constant which is related to the relative dispersion and which we propose to call the dispersiometric coefficient D_{FC}:

$$D_{FC} = \frac{n_F - n_C}{n_C - 1.04} \cdot 10^4. \tag{6}$$

It would be expected that the new refractometric constant (6), combining, as it does, the merits of specific (1) and relative (2) dispersions, will be even more convenient for the analysis of petroleum by the dispersion method.

In Table 4 are presented values of D_{FC} calculated from the same original experimental data presented in Table 2, and these values indicate the very high degree of constancy of the dispersiometric coefficient for all of the dearomatized fractions investigated.

The average values of D_{FC} for gasoline and kerosene fractions agree within the limits of accuracy of the measurements. The deviation from the average value was only 0.4%, which is less than for previously used refractive dispersion functions. The divergence between the maximum and minimum values of D_{FC} was only 2% instead of the 3.5% for ω_{FC}, the 2.6% for δ_{FC}, the 5.3% for ω_R and 8.8% for δ_R.

The data indicate the desirability of using the new constant—the dispersiometric coefficient—for the investigation of petroleum fractions.

SUMMARY

1. Measurement of the dispersion of gasoline-kerosene fractions of 47 different petroleums showed that values of δ_R (3) and ω_R (4) for dearomatized fractions display considerable variation and cannot be recommended for analysis by the dispersion method.

2. The average value of the specific dispersion δ_{FC} (1) for dearomatized gasoline fractions was 97.3, which is appreciably less than the previously used value of 98-99. The average value of the relative dispersion ω_{FC} (2) of the dearomatized fractions with a boiling range of up to 200° is in agreement with the earlier value of 17.55 [3].

3. In investigations of petroleum, it is expedient to use a new constant—the dispersiometric coefficient $D_{FC} = \frac{n_F - n_C}{n_C - 1.04} \cdot 10^4$, which is distinguished by an exceptionally high constancy for dearomatized fractions and which excels in this respect all other formulas for refractive dispersion. The dispersiometric coefficient of dearomatized fractions boiling up to 300° has an average value of 194.4 ± 0.8.

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LOW-TEMPERATURE OXIDATION PRODUCTS IN DIESEL FUELS

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It is well known that diesel fuels as a rule have a color ranging from light to dark yellow owing to the presence of gum. The latter are chiefly oxidation products of hydrocarbons which have been oxidized to some extent or other. Until fairly recently, the gum content of diesel fuels has not been controlled. Therefore, the literature contains only very little information either on the quantitative content of gum in diesel fuels or on the gum's nature. Moreover, gum, which is formed in diesel fuel during storage, may be the principal cause of the formation of deposits on the needles or injection valves of diesel engines [1].

Sergienko and Galich [2], during an investigation of the behavior of diesel fuels during storage in small glass flasks which were exposed to light, established that there is an appreciable increase in the gum content of diesel fuels during storage over a period of from two to five years. Moreover, they noted that the aromatic hydrocarbons present in the fuel are the worst gum formers, and these aromatics are the principal source of gum-forming processes in diesel fuels. The naphthene–isoparaffin hydrocarbons separated from this same straight-run diesel fuel were subjected to low-temperature oxidation conditions, and it was found that oxidation of these hydrocarbons had a greater induction period; no gum was detected in them after a two-year storage, but the content of peroxide compounds, the initial oxidation products, was high.

Detailed investigations of the products of the low-temperature oxidation of straight-run and cracked light naphtha-kerosene fractions have been carried out by Chertkov and Zrelov [3-5], who established that aromatic hydrocarbons with unsaturated aliphatic side chains are the first compounds to undergo oxidation. Moreover, the oxidation products are chiefly alcohols and carbonyl compounds, and acidic and highly condensed compounds are present only in small amounts.

The gums contained in fuels are a mixture of oxygenated compounds of different types. According to the data of Sergienko and Galich [2], the molecular weight of the gum exceeds the molecular weight of the hydrocarbons composing the fuel by a factor of approximately 1.5, while the molecular weight of the asphaltenes formed in the fuel during storage exceeds that of the hydrocarbons by a factor of almost two. The oxygenated compounds isolated by Chertkov and Zrelov differed comparatively little with respect to molecular weight from the hydrocarbons from which they were formed.

We considered it desirable to investigate the nature not of the total gum formed in diesel fuel during storage under normal conditions, but rather the nature of fractions of the gum separated by adsorption.

Five samples of diesel fuels of different origin and which had been stored for two to three years were used in the investigation; these fuels were two straight-run sulfur-free fuels, DZ and DL by GOST 4749-49, a straight run, high-sulfur diesel fuel (sulfur content, 1%), a catalytically cracked diesel fuel (DTK), and a diesel fuel obtained by hydrogenation of coal tar (synthetic).

In Table 1 are presented the physicochemical properties of the fuels, and Table 2 presents their hydrocarbon group composition. The latter was determined by a combination of chromatographic separation of portions of the fuel with 65-150-mesh silica gel into a paraffin–naphthene fraction and an aromatic fraction and group structural analysis of the two fractions by the M-n_D^{20} method [6]. The content of unsaturated hydrocarbons was calculated from the iodine number as determined by GOST 2070-55; for this determination, the fuel was dissolved in acetone.

TABLE 1

Physicochemical Properties of the Fuels Investigated

Fuel	Density d_4^{20}	Distillation data					Actual gum by GOST 8489-57 (in mg/100 ml)	Sulfur content (in %)	Temperature (°C)		Viscosity at 20° (in centistokes)	Acidity (in mg KOH per 100 ml
		IBP	10%	50%	90%	96%			sediment	pour point		
Diesel fuel DL by GOST 4749-49	0.861	195°	220°	275°	342°	348°	41	0.024	—10	—20	5.9	3.25
Diesel fuel DZ by GOST 4749-49	0.850	187°	206°	254°	316°	360°	79	0.09	—50	—60	4.42	3.94
High-sulfur diesel fuel (1.0% sulfur)	—	205°	240°	273°	327°	348°	27	1.0	—2	—12	5.39	2.85
Synthetic diesel fuel	0.856	202°	222°	256°	330°	—	42	0.035	—	—26	4.2	4.1
Catalytic diesel fuel	0.875	237°	252°	270°	314°	340°	56	0.13	—21	—23	5.05	3.67

In any consideration of Table 2, the high content of aromatic hydrocarbons in the catalytic and synthetic fuels is noteworthy; furthermore, the aromatic hydrocarbons in the catalytic fuel were principally bicyclic, while in the synthetic fuel they were exclusively monocyclic. The content of unsaturated hydrocarbons in the fuels was not large and did not exceed 4.0%.

The gum, or oxygenated compounds, was separated from the fuels by chromatography over aluminum oxide. The hydrocarbon fraction was desorbed with isopentane, and desorption of the oxygenated compounds was accomplished by four successive desorbents: carbon tetrachloride, benzene, acetone, and an alcohol-benzene mixture (1 : 1). Oxygenated compounds present in the catalytic fuel were not completely desorbed by the alcohol-benzene mixture. Therefore, acetic acid, recommended by Z. A. Sablina, was used for complete desorption of the oxygenated compounds.

It may be assumed that the use of several desorbents separated the oxygenated compounds according to their extent of oxidation, and that with increasing polarity of the desorbent, the more deeply oxidized compounds were desorbed.

After distillation of the desorbent in a stream of nitrogen, the resulting oxygenated compounds were characterized by molecular weight, iodine number, acid number, elemental composition, and index of refraction.

Table 3 presents data on the content of the various fractions of oxygenated compounds in the fuels, as separated by the various desorbents, and Table 4 gives their characteristics.

It may be seen from these data that the over-all content of oxygenated compounds in the fuels investigated varied within wide limits—from 0.75 to 3.29%. The lowest amount, less than 1.0%, was present in the sulfur-free, straight-run fuels, and the greatest amount was present in the synthetic fuel. The catalytic and high-sulfur fuels had high contents of oxygenated compounds.

A high content of oxygenated compounds does not permit unequivocal characterization of the depth of oxidation of fuel, since these compounds can be, to a considerable extent, initial oxidation products formed over a brief period of time from the unstable components of the fuel. The distribution of the oxidation products throughout the fractions gives a better idea of the depth of oxidation of the fuel.

The fuels investigated differed from each other not only with respect to the total amount of oxygenated compounds, but also with respect to the distribution of these compounds among the individual fractions.

TABLE 2

Hydrocarbon Group Composition of the Fuels Investigated

Fuel	Chromatographic analysis						Paraffinic hydrocarbons in side chains (in %)	Structural analysis				Content of unsaturated hydrocarbons (in %)
	paraffin-naphthene fraction			aromatic fraction				naphthene rings		aromatic rings		
	content in fuel (in %)	mol. wt.	refractive indices n_D^{20}	content in fuel (in %)	mol. wt.	refractive indices n_D^{20}		No. in molecule	wt. in fuel (in %)	No. in molecule	wt. in fuel (in %)	
Diesel fuel DL	93.9	218	1.4568	5.4	210	1.5218	38.2	1.08	38.5	1.48	2.6	—
Diesel fuel DZ	78.3	185	1.4548	18.0	163	1.5420	44.5	1.14	39.2	1.56	12.6	-
High-sulfur diesel fuel	76.4	220	1.4450	22.1	190	1.5340	67.6	0.55	17.6	1.58	13.3	1.5
Synthetic diesel fuel	72.0	188.3	1.4480	27.8	154.5	1.4857	56.5	0.9	30.2	0.94	13.1	4.0
Catalytic diesel fuel	73.4	190	1.4543	25.9	155	1.5840	41.0	1.1	36.0	1.86	22.3	3.0

With the exception of the oxygenated compounds desorbed by benzene, the content of which in the fuels varied within narrow limits (0.16-0.32%), the contents of all remaining fractions of oxygenated compounds varied over a rather wide range.

The catalytic fuel differed from the other fuels in the presence of oxygenated compounds desorbed by acetic acid, and the synthetic fuel differed in its sharply increased content of oxygenated compounds desorbed by the alcohol-benzene mixture. A relatively large amount of the latter type was present in the catalytic fuel. Such compounds were present in the DL and DZ fuels in very small amounts. These fuels also contained the lowest amounts of oxygenated compounds desorbed by acetone and carbon tetrachloride. Once again, the synthetic fuel contained a sharply increased amount of oxidation products desorbed by acetone.

It should be remarked that part of the oxygenated compounds distilled during the distillation of the acetone from the oxygenated compounds in a stream of nitrogen. The amount of this distilled portion was associated directly with the amount of oxidation products desorbed by the alcohol-benzene mixture, i.e., with the degree of oxidation of the fuel, and it amounted to 4% for the DL fuel, 12% for the DZ fuel, 16% for the high-sulfur fuel, and 30% for the catalytic fuel, these figures being based on the total amount of this fraction of oxidation products.

The data of Table 4 show that there was a general regularity in the change of the nature of oxygenated products from fraction to fraction, a regularity which was characteristic of all of the fuels investigated; this confirms the assumption made above as to the degree of oxidation of the individual fractions and, partially, as to their nature.

For all of the fuels, the minimum oxygen content occurred in the oxygenated compounds desorbed by carbon tetrachloride. The content of oxygen was higher, but, as a rule, insignificantly, in the oxygenated compounds desorbed by benzene. There was a sharp increase in oxygen content of the oxygenated compounds desorbed by acetone and by the alcohol-benzene mixture, amounting, in individual cases, to almost two atoms per molecule of oxygenated compound. Moreover, in some of the fuels a larger amount of oxygen was present in the compounds desorbed by acetone, while in others a larger amount of oxygen was present in the compounds desorbed by the alcohol-benzene mixture. The oxygen content of the oxygenated compounds desorbed by acetic acid was higher than that of the compounds desorbed by the alcohol-benzene mixture. The sulfur content of the individual fractions of oxygenated compounds was in conformity with the sulfur contents of the original fuels.

TABLE 3

Content of the Individual Fractions of Oxygenated Compounds in the Fuels

Fuel	Content of adsorbed gum (in %)					
	total	by fractions				
		carbon tetrachloride	benzene	acetone	alcohol-benzene mixture	acetic acid
Diesel fuel DL	0.735	0.32	0.13	0.28	0.015	0
Diesel fuel DZ	0.924	0.16	0.14	0.60	0.024	0
High-sulfur diesel fuel	2.033	0.85	0.18	0.95	0.043	0
Synthetic diesel fuel	3.29	0.68	0.23	1.70	0.68	0
Catalytic diesel fuel	1.864	0.77	0.20	0.75	0.12	0.024

Thus, all of the fractions of oxygenated compounds extracted from the high-sulfur fuel contained sulfur. The content was about 0.055%, calculated on the fuel. The sulfur present in the fractions of oxygenated compounds obtained from the catalytic fuel was approximately 0.02%, calculated on the basis of the fuel, and it amounted to approximately 0.017 and 0.005%, respectively, for the DZ and DL fuels.

A characteristic of all fractions of oxygenated compounds separated from the various fuels was their molecular weights, which differed little from the molecular weights of the respective fuels. Thus, the molecular weight of the DL fuel was 215, and the molecular weights of the oxygenated compounds separated from it varied within the limits 172-259•; for the high-sulfur fuel, these values were, respectively, 206 and 181-266; for the catalytic fuel, they were 187 and 210-238; and for the synthetic fuel, they were 193 and 231-250. The empirical formulas calculated from the molecular weights and elemental compositions of the individual fractions of oxygenated compounds show that, with the exception of that part of the acetone-desorbed oxygenated compounds which distilled, these oxygenated compounds contained an average of only 10 to 18 carbon atoms per molecule, i.e., even fewer, in certain cases, than the number contained in a molecule of the hydrocarbons forming the diesel fuels. This indicates that the oxidation process proceeding at low temperatures during the storage of diesel fuels is not accompanied by polymerization of oxygenated compounds, in spite of the fact that in a number of cases these compounds are highly unsaturated.

The difference between our data on the molecular weight of the oxygenated compounds and the data obtained by Sergienko and Galich can apparently be explained by the difference in oxidation conditions, since they stored their fuels in small glass flasks located by a window, i.e., subject to the action of light. It is well known that light not only intensifies oxidative processes, but also modifies their course. In particular, it is possible that the role of polymerization processes is increased under the influence of light. It is noteworthy that the oxidation products separated by Chertkov and Zrelov from light naphtha-kerosene fractions contained an average of 10-12 carbon atoms per molecule; this is approximately the same as in the original hydrocarbons. In other words, during storage in an iron container, i.e., without the influence of light, appreciable polymerization or condensation of the oxidation products is not observed, even in the case of such fractions as a cracked kerosene.

As would be expected, the oxygenated compounds obtained from all of the fuels investigated by desorption with alcohol-benzene mixture had high acid numbers; this was also true of their iodine numbers. This fact, and also the combination of high acid number with high iodine number, indicates that during low-temperature oxidation, compounds with an unsaturated bond preferentially undergo oxidation, and the addition of oxygen does not take place at the double bond.

The significantly lower acid number of all fractions of oxygenated compounds separated from the high-sulfur diesel fuel merits mention.

• These figures do not take into account that part of the acetone-desorbed oxygenated compounds which distilled.

TABLE 4

Characteristics of the Oxygenated Compounds Separated from the Fuels

Fuel	Oxygenated-compound fraction	Mol. wt.	Number		Refractive index	Elemental composition				C/H ratio	Empirical formula
			iodine	acid		C	H	S	O (by difference)		
Diesel fuel DL	Carbon tetrachloride	259	55.7	15.3	1.6967	88.54	8.59	1.64	1.23	10.3	$C_{18.4}H_{22.2}O_{0.2}S_{0.13}$
	Benzene	238	88.9	13.3	1.6530	88.64	9.22	0	2.14	9.6	$C_{17.3}H_{22.0}O_{0.32}$
	Acetone (undistilled part)	249	68.9	15.7	1.6925	78.51	10.54	0	17.95	7.5	$C_{16.3}H_{26.2}O_{1.94}$
	Acetone (distilled part)	119	—	—	—	—	—	—	—	—	—
	Alcohol-benzene mixture	172	99.3	45.0	—	75.97	9.31	0	14.72	7.16	$C_{10.05}H_{16.0}O_{1.58}$
Synthetic diesel fuel	Carbon tetrachloride	259	27.9	22.5	1.6488	84.75	11.6	0	3.65	7.3	$C_{18.3}H_{30.0}O_{0.59}$
	Benzene	245	67.2	25.1	1.6522	81.62	9.87	0	8.51	8.25	$C_{16.6}H_{24.2}O_{1.3}$
	Acetone (undistilled part)	215	62.6	14.9	1.6960	73.79	10.51	2.08	13.62	7.05	$C_{13.1}H_{22.6}S_{0.14}O_{1.84}$
	Acetone (distilled part)	113	14.65	1.1	1.4250	—	—	—	—	—	—
	Alcohol-benzene mixture	233	96.8	42.5	—	73.09	9.17	4.25	13.42	7.99	$C_{14.2}H_{21.4}S_{0.31}O_{1.96}$
High-sulfur diesel fuel	Carbon tetrachloride	181	69.0	4.1	1.6915	84.56	8.57	3.76	3.11	9.87	$C_{12.75}H_{15.5}S_{0.29}O_{0.35}$
	Benzene	223	144.8	3.0	1.6550	84.06	10.88	1.64	3.42	7.72	$C_{13.7}H_{24.2}S_{0.11}O_{0.48}$
	Acetone (undistilled part)	266	141.4	3.4	1.6923	80.17	10.59	2.15	7.09	7.57	$C_{17.3}H_{26.9}S_{0.18}O_{1.18}$
	Acetone (distilled part)	103	—	1.2	1.4317	63.04	10.38	0.57	26.0	6.07	$C_{5.41}H_{10.75}S_{0.18}O_{1.68}$
	Alcohol-benzene mixture	191	54.5	14.4	1.6580	76.19	9.65	2.06	12.7	7.9	$C_{12.2}H_{18.4}S_{0.12}O_{1.53}$
Catalytic diesel fuel	Carbon tetrachloride	215	82.3	13.6	1.6970	91.25	8.15	0	0.6	11.19	$C_{16.38}H_{17.55}O_{0.08}$
	Benzene	216	71.9	33.2	—	90.72	7.28	0.75	1.25	12.4	$C_{16.35}H_{15.74}O_{0.17}$
	Acetone (undistilled part)	238	42.6	49.8	1.6972	80.07	8.77	1.79	9.37	9.15	$C_{15.2}H_{19.99}S_{0.13}O_{1.39}$
	Acetone (distilled part)	133	4.2	5.8	1.4355	—	—	—	—	—	—
	Alcohol-benzene mixture	210	155.3	133.0	—	74.09	8.34	4.18	13.39	8.89	$C_{13.6}H_{17.6}S_{0.27}O_{1.72}$
	Acetic acid	219	38.0	—	—	75.55	10.47	0	13.98	7.2	$C_{15.8}H_{19.12}O_{1.91}$
Synthetic diesel fuel	Carbon tetrachloride	250	—	—	1.6048	—	—	—	—	—	—
	Benzene	—	—	—	1.5985	—	—	—	—	—	—
	Acetone (undistilled part)	213	—	—	1.5319	—	—	—	—	—	—
	Acetone (distilled part)		—	—							
	Alcohol-benzene mixture	250	63.0	—	1.5190	—	—	—	—	—	—

The oxygenated compounds separated from all of the fuels had high indices of refraction. The only exception was the distillable part of the oxygenated compounds desorbed by acetone. The presence of the latter was apparently the result of cleavage processes occurring during the low-temperature oxidation. The values of the indices of refraction indicate the presence mainly of two aromatic rings or of a naphthene-aromatic ring in the molecules of the oxygenated compounds separated from the DL and DZ diesel fuels, the high-sulfur fuel, and the catalytic fuel, and predominantly one aromatic ring in the oxygenated compounds separated from the synthetic fuel.

This aromatic-ring structure of the oxygenated compounds corresponds to the aromatic-ring structure of the hydrocarbons composing the fuels. The aromatic hydrocarbons in the catalytic fuel contained the greatest number of rings. The oxygenated compounds separated from this fuel had the highest carbon-to-hydrogen ratio, especially in the fractions desorbed by carbon tetrachloride and benzene. The carbon-to-hydrogen ratio and the empirical formula calculated from the elemental composition and molecular weight also indicate the presence of more than one aromatic or naphthene-aromatic ring in the molecule of the oxygenated compounds obtained from the DZ and DL diesel fuels and from the high-sulfur fuel, and they also indicate even more than two aromatic rings in the carbon tetrachloride- and benzene-desorbed oxygenated compounds in the catalytic fuel.

The high iodine number of the oxygenated compounds separated from the various diesel fuels and the aromatic character of their hydrocarbon parts show that, as in the case of kerosenes, aromatic hydrocarbons having a double bond in an aliphatic side chain are the first components of a diesel fuel to undergo low-temperature oxidation.

SUMMARY

1. During low-temperature oxidation of diesel fuels occurring during prolonged storage, the oxidation processes are not accompanied by polymerization of the oxygenated compounds in spite of the unsaturated character of the latter.

2. At low temperatures, aromatic hydrocarbons having a double bond in an aliphatic side chain are the first components of diesel fuels to undergo oxidation.

3. The number of aromatic rings in the oxygenated compounds corresponds to the number contained in the hydrocarbons forming the diesel fuels subjected to low-temperature oxidation.

4. The over-all content of oxygenated compounds in the fuels investigated, varied within wide limits—from 0.75 to 3.29%. The lowest amount—less than 1.0%—was present in the sulfur-free straight-run diesel fuels, while the greatest amount—3.29%—was contained in the synthetic fuel obtained by hydrogenation of coal tar.

5. With the exception of the oxygenated compounds desorbed by benzene, which were present in all of the fuels investigated in approximately equal amounts, the content of oxygenated compounds desorbed by carbon tetrachloride, acetone, and alcohol-benzene mixture varied within a wide range.

The synthetic fuel differed from the remaining fuels by its especially high content of oxygenated compounds desorbed by acetone (1.7%) and by alcohol-benzene mixture (0.68%), and the catalytic diesel fuel was distinguished by the presence of oxygenated compounds desorbed by acetic acid.

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CATALYTIC CONVERSIONS OF PARAFFIN ON GUMBRINE

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In contrast to the work published previously [1], the present work on the catalytic conversion of petroleum paraffin was carried out with a different ratio between the product and the catalyst and this made it possible to lower the reaction temperature considerably. In addition, the use of new methods made it possible to study the chemical nature of the conversion products obtained more thoroughly.

EXPERIMENTAL

For the experiments we used commercial paraffin which was first purified thoroughly with sulfuric acid. The physicochemical characteristics of the purified paraffin are given in Table 1. The same table gives the composition of the paraffin from the thermocatalysis products. The paraffin did not contain aromatic hydrocarbons. The paraffin conversion was carried out at atmospheric pressure in a metal reactor column at a temperature up to 250° and a ratio of product to catalyst of 1 : 5 The catalyst was the natural clay, gumbrine, activated with hydrochloric acid and dried at 120° for 3 hours. Rapid decomposition of the paraffin occurred even at 185°. The yields of products from the thermocatalytic conversion of paraffin are given in Table 2. Fractions of hydrocarbons boiling at 200-250° and 400-500° were obtained in the greatest yield.

Investigation of products from thermocatalysis of paraffin. The gaseous products consisted mainly of methane with a small amount of its gaseous homologs and unsaturated hydrocarbons. The liquid products did not

TABLE 1

Physicochemical Properties of Starting Paraffin and Paraffin from Thermocatalysis

Product	Amount of paraffin (%) in reaction with urea		Melting point (°C)	n_D^{70}	d_4^{70}	M	Elementary formula			C/H	Empirical formula	General formula of series
	giving complex ("normal")	not giving complex ("isomer")					C	H	S			
Starting paraffin	75	25	61	1.4386	0.7892	460	85.22	14.62	0.09	5.82	$C_{32.7}H_{66.9}$	$C_nH_{2n+1.5}$
"Normal"	—	—	64	1.4370	0.7869	440	85.18	14.75	—	5.77	$C_{31.2}H_{64.4}$	C_nH_{2n+2}
"Isomer"	—	—	50.5	1.4436	0.8055	485	85.48	14.60	—	5.85	$C_{34.52}H_{70.24}$	$C_nH_{2n+1.2}$
Paraffin from thermocatalysis	60	40	61.5	1.4364	0.7878	420	85.24	14.77	—	5.77	$C_{29.66}H_{61.54}$	C_nH_{2n+2}
"Normal" from thermocatalysis	—	—	64	1.4370	0.7871	432	85.21	14.77	—	5.77	$C_{30.67}H_{63.3}$	C_nH_{2n+2}
"Isomer" from thermocatalysis	—	—	56.5	1.4363	0.7888	402	85.25	14.80	—	5.76	$C_{28.5}H_{59}$	C_nH_{2n+2}

TABLE 2

Yields of Products from Thermocatalysis of Paraffin

Fraction	Yield relative to starting material (in wt. %)	Molecular wt. of fraction after removal of aromatics
Gaseous hydrocarbons	3.8	—
28—65°	5.0	80
65—95°	4.7	91
95—122°	5.4	107
122—150°	6.5	119
155—200°	8.0	145
200—250°	10.5	176
250—300°	4.4	218
300—400°	5.2	286
400—500°	8.9	420
Above 500°	1.4	479
Solid hydrocarbons	20.5	420
Alcohol-benzene resins	9.5	—
Carbon on clay	4.6	—
Experimental bases	1.6	—

contain unsaturated hydrocarbons and began to boil at 28°, which corresponds to pentane. In hydrocarbon group composition (Table 3), determined by the aniline method, the liquid products consisted of methane hydrocarbons (56.6%) and naphthenes (0.5%), while the aromatic fraction corresponded to 2.9% of the original paraffin. The first fractions consisted wholly of isomerization products and hydrocarbons giving a complex with urea only appeared beginning with the fraction boiling at 250-300°.

Aromatic hydrocarbons were isolated from fractions boiling at 150-200°, 200-250, 250-300, and above 300° by chromatographic adsorption on silica gel.

According to structural group analysis (Table 4), the aromatic concentrates consisted of monocyclic, bicyclic, and a small amount of tricyclic hydrocarbons with a large number of substituents. The amount of carbon in the paraffin structures reached 40% of the total content. Naphthene rings were absent from the aromatic hydrocarbons.

The characteristics of the solid hydrocarbons from the thermocatalysis as compared with the starting paraffin are given in Table 1. The data presented indicate that the part of the starting paraffin that does not give a complex with urea is converted; normal hydrocarbons of the starting paraffin are also converted into isoparaffins, both solid and liquid, of similar molecular weight.

The solid, normal hydrocarbons from the thermocatalysis were part of the normal hydrocarbons of the starting paraffin that had not reacted. Their identity was demonstrated by the agreement of the physicochemical properties.

DISCUSSION OF RESULTS

According to theory, methane hydrocarbons undergo the following conversions: a) isomethanes with a tertiary carbon atom are readily cleaved to form CH_4; b) normal methane hydrocarbons undergo isomerization (a peculiar process of hydrogen redistribution inside the molecule, reducing its free-energy level); c) under the action of temperature and a catalyst there is cleavage of high-molecular methane hydrocarbons with rupture of a C—C bond, predominantly in the middle of the molecule.

In paraffin, which is a mixture of hydrocarbons of various molecular weights and structures, there is simultaneous isomerization and cleavage to form various methane hydrocarbons—gases, liquids and solids.

The source of aromatic hydrocarbons could be: a) olefins (as any catalytic cleavage of methane hydrocarbons passes through the stage of olefin + aliphatic hydrocarbon), which are cyclized to aromatic hydrocarbons; b) according to thermodynamic considerations [3], the conversion of high-molecular methane hydrocarbons into aromatics without the stage of olefins is quite probable.

TABLE 3

Hydrocarbon Group Composition of Fractions

Take-off temperature range of fraction (in °C)	Yield of fraction relative to starting material (wt. %)	Maximum aniline point (°C)		Amount of hydrocarbons (in wt. %)					
		before removal of aromatics	after removal of aromatics	on fraction	on starting paraffin	on fraction	on starting paraffin	on fraction	on starting paraffin
28—65	5.0	—	—	—	—	—	—	100	5
65—95	4.7	68.9	69.0	0.1	0	5	0.2	94.9	4.5
95—122	5.4	69.0	69.7	0.8	0	4.2	0.2	95	5.3
122—150	6.5	70.0	72.5	3.1	0.2	2.4	0.1	94.5	6.1
150—200	8.0	72.9	78.8	9.1	0.7	0	0	90.9	7.3
200—250	10.5	81.9	86.2	7.5	0.8	0	0	92.5	9.7
250—300	4.4	90.4	93.8	6.5	0.3	0	0	93.5	4.1
Above 300	15.5	113.8	116.6	5.9	0.9	0	0	94.1	14.6
Total	60.0	—	—	—	2.9		0.5		56.6

TABLE 4

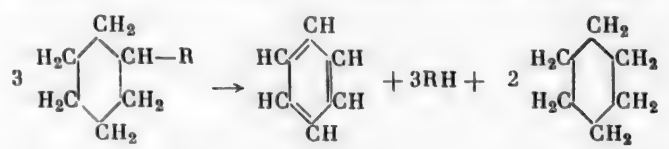
Physicochemical Characteristics of Aromatic Concentrates

Fraction (°C)	n_D^{20}	d_4^{20}	M	Structural group analysis by the n-d-M method, modified by Hazelwood [2]					Specific dispersion	$n-\frac{d}{2}$	General formula of series
				hydrogen content			No. of rings				
				C_A	C_H	C_n	R_A	R_H			
150—200	1.4851	0.8398	135	—	—	—	—	—	137	1.0652	C_nH_{2n-4}
200—250	1.5080	0.8758	156	53	7	40	1.0	0.2	178	1.0701	—
250—300	1.5458	0.9190	187	59	2	39	1.53	0.07	209	1.0863	—
Above 300	1.5848	0.9731	287	59	0	41	2.64	0	253	1.0983	$C_nH_{2n-14.7}$

In contrast to hydrocarbons isolated from natural petroleum [4], the aromatic hydrocarbons obtained did not contain hybrid forms with aromatic and naphthene rings when both have a large number of methane substituents.

Under the conditions of thermocatalysis naphthene hydrocarbons undergo the following conversions: On one hand, naphthenes can lose hydrogen comparatively readily, forming aromatic structures, and on the other hand, under the action of hydrogen, naphthene rings tend to open, with rupture of a C—C bond and the formation of methane chains; naphthenes with high-molecular substituents tend to isomerize to form naphthenes with short substituents.

In addition, we can assume the conversion of naphthenes according to the scheme



with the redistribution of hydrogen inside the molecule leading to the formation of aromatic, methane, and simple naphthene hydrocarbons. This reaction route is proved by the presence of a small amount of naphthenes in the

light fractions of the thermocatalysis products. The presence of naphthene hydrocarbons in the light fractions from thermocatalysis of paraffin and ceresin was observed by Zelinskii and Mikhlina [5], Dobryanskii and Vorob'eva [6], and Bogomolov and Smirnova [1]. As according to the results of elementary analysis and the general formula $C_nH_{2n\pm x}$, ceresin contains more naphthene rings, it gives a larger amount of naphthenes in the conversion products. Regeneration of naphthenes does not occur during the thermocatalysis of paraffin.

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CONTINUOUS NITRATION OF ETHYLBENZENE

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There is literature on the continuous nitration of benzene, toluene, and other aromatic and aliphatic compounds. It is known that the productivity of continuous nitration apparatus is considerably greater than that of batch-operating apparatus. We should also note that well-developed, continuous nitration processes give nitro compounds of better quality.

Despite the fact that a large quantity of p-nitroethylbenzene is used in a number of countries as an intermediate in the production of the synthetic antibiotic levomycetin (or its racemate, synthomycin), no continuous methods of mononitrating ethylbenzene have been described.

We developed the continuous nitration of ethylbenzene to nitroethylbenzene (abbreviation for a mixture of p-, o-, and m-nitroethylbenzenes) with a nitration mixture of nitric and sulfuric acids on the principle of a direct-flow system.

The proposed method is based on the optimal conditions found for the batch mononitration of ethylbenzene [1]. The following optimal conditions were established for batch nitration of ethylbenzene to nitroethylbenzene: the activity factor of the nitrating mixture (F) 72-73%, 5% excess of nitric acid over the amount required theoretically, temperature on adding the nitrating mixture to the ethylbenzene 45-50°, temperature of nitration mixture 50-55°, time of adding nitrating mixture 15-20 minutes, and reaction time 30 minutes.

Many factors were not changed in the development of the continuous nitration of ethylbenzene. Only the effect of an excess of nitric acid from 1 to 5% on the yield and quality of the nitroethylbenzene and the mixing temperature of the components in the main nitrator over the ranges 40-45 and 45-50° were checked.

We found the optimal conditions for the continuous nitration of ethyl-benzene to nitroethylbenzene by the method described in the experimental section of this article. The ethylbenzene was nitrated in two apparatuses connected in series. The design of nitration apparatus we chose did not differ in principle from those used industrially, which operate on the direct current principle described in the monograph by Vorozhtsov [2]. The only difference was that instead of a propellor stirrer, a turbine type was used and the components were mixed in the upper instead of the lower part of the nitrator. The continuous addition of ethylbenzene and nitrating mixture was at rates calculated for the nitration mixture remaining in the nitration system for 1 hour (30 minutes in each apparatus). The nitration mixture from the buffer nitrator was collected in a receiver for 1 or 2 hours and weighed. The nitration product was separated from the spent acid, and the nitroethylbenzene and spent acid were also weighed and analyzed. The nitroethylbenzene was checked for specific gravity, acidity, and ethylbenzene and dinitroethylbenzene contents. This data was used to calculate the mononitroethylbenzene yield relative to the ethylbenzene taken for the reaction. The results of the most characteristic experiments on the continuous nitration of ethylbenzene are given in Table 1.

From several experiments with continuous input of components for from 11 to 16.5 hours, we established that the optimal conditions for continuous nitration of ethylbenzene to nitroethylbenzene are as follows: a nitrating mixture activity factor of 72-73%, a nitric acid excess of 5%, a temperature of 40-45° in the main nitrator, 50-55° in the buffer nitrator, and the nitration mixture remaining 30 minutes in each apparatus.

TABLE 1

Experimental Results of Continuous Nitration of Ethylbenzene to Nitroethylbenzene

Expt. No.	Charge (in g)		Nitrating mixture (%)		Activity factor of nitrating mixture (in %)	HNO_3 excess (in %)	Experiment duration (in hr)	Sample take-off time (in hr)	Spent acid composition (in %)				Material obtained (g)		Acidity of nitroethylbenzene (%)	Yield pure nitroethylbenzene		Specific gravity of nitroethylbenzene	Content (in %)	
	ethylbenzene	nitrating mixture	H_2SO_4	HNO_3					H_2SO_4	HNO_3	N_2O_3	nitro compound	spent acid	nitroethylbenzene		mg	% of theoretical		ethylbenzene	dinitroethylbenzene
1	2416	6510	60.81	23.16	72.8	5.0	11.2	2	72.61	0.41	0.23	0.23	—	—	—	—	—	1.122	1.02	None
								3	72.53	1.21	0.24	0.15	—	—	—	—	—	—	0.21	—
								4	72.63	0.78	0.21	0.11	—	—	—	—	—	—	—	—
								5	72.68	1.27	0.21	0.14	—	—	—	—	—	—	—	—
								6	72.98	1.31	0.28	0.09	—	—	—	—	—	1.120	None	None
								7	72.71	0.51	0.23	0.09	—	—	—	—	—	—	None	—
								8	72.35	1.44	0.25	0.11	—	—	—	—	—	—	—	—
								9	71.82	1.80	0.28	0.13	—	—	—	—	—	1.122	—	None
								10	72.20	1.52	0.22	0.15	—	—	—	—	—	—	—	—
								11	72.93	0.82	0.20	0.11	5480	3438	0.72	3414	99.2	1.122	—	None
2	3125	8651	60.79	22.20	72.3	3.5	16.4	2	—	—	—	0.06	—	—	—	—	—	—	2.39	
								4	71.43	0.41	0.37	0.04	—	—	—	—	—	—	2.76	
								6	71.55	0.51	0.31	0.10	—	—	—	—	—	—	4.81	
								8	71.44	0.95	0.31	0.13	—	—	—	—	—	—	3.11	
								10	71.40	0.73	0.32	0.06	—	—	—	—	—	—	1.66	
								12	71.37	0.65	0.32	0.06	—	—	—	—	—	—	2.26	
								14	71.66	0.52	0.32	0.07	—	—	—	—	—	—	2.11	
								16	71.69	0.51	0.30	0.05	7303	4453	0.61	4427	99.5	1.120	1.49	None
3	3135	8594	61.33	21.76	72.55	1.0	15.0	1	71.75	0.40	0.30	0.06	—	—	—	—	—	—	2.50	
								3	71.59	0.48	0.60	0.05	—	—	—	—	—	—	1.62	
								5	71.98	0.16	0.37	0.02	—	—	—	—	—	—	0.98	
								7	71.84	0.34	0.32	0.03	—	—	—	—	—	—	1.58	
								9	71.91	0.32	0.32	0.04	—	—	—	—	—	—	1.77	
								11	72.25	0.24	0.10	0.03	—	—	—	—	—	—	1.39	
								13	71.89	0.33	0.31	0.03	—	—	—	—	—	—	1.59	
								15	72.58	0.28	0.34	0.03	7200	4496	0.82	4459	99.8	1.120	1.64	

TABLE 2

Cyclic Experiments on the Washing of Acid Nitroethylbenzene

No. of cycles of wash water	Nitroethylbenzene used		Amount of water (in ml)									Acidity of washed nitroethylbenzene (in %)
			stage I of wash				stage II of wash			stage III of wash		
	weight (in g)	acidity (in %)	wash water I	wash water II	fresh water	acidity of wash water I (in %)	wash water II	wash water III	fresh water	wash water III	fresh water	
—	100	1.16	—	—	400	0.23	—	—	400	—	400	0.028
1	100	1.16	365	20	—	0.52	365	20	—	363	20	0.11
2	100	1.16	340	20	—	0.77	345	20	—	345	20	0.15
3	100	1.16	325	20	—	1.00	330	20	—	335	20	0.12
4	100	1.16	350	20	30	1.06	350	20	30	320	80	0.11
5	100	1.16	380	20	—	1.23	380	20	—	360	40	0.10
6	100	1.16	360	20	20	1.36	365	20	15	360	40	0.09
7	100	1.16	365	20	15	1.48	365	20	15	375	25	0.08
8	100	1.16	360	20	20	1.55	360	20	20	360	40	0.08
9	100	1.16	360	20	15	1.64	360	20	15	370	30	0.08
10	100	1.16	360	20	20	1.68	360	20	20	365	35	0.08
11	100	1.16	365	20	15	1.75	360	20	20	365	35	0.08
12	100	1.16	365	20	15	1.82	360	20	20	355	45	0.08
13	100	1.16	365	20	15	1.89	365	20	15	360	40	0.08
14	100	0.72	365	20	15	1.98	365	20	15	365	35	0.12
15	100	0.72	360	20	20	2.03	365	20	15	365	35	0.12
16	100	0.72	370	20	10	2.17	365	20	15	365	35	0.13
17	100	0.72	365	20	15	2.28	360	20	20	360	40	0.13
18	100	0.72	360	20	20	2.38	365	20	15	360	40	0.13
19	100	0.72	360	20	20	2.45	365	20	15	360	40	0.12
20	100	0.72	360	20	20	3.02	360	20	20	365	35	0.11
21	100	0.72	365	20	15	2.98	360	20	20	365	35	0.09
22	100	0.72	365	20	15	2.94	365	20	15	365	35	0.09
23	100	0.72	360	20	20	2.88	360	20	20	365	35	0.10
24	100	0.72	365	20	15	2.77	365	20	15	365	35	0.10
25	100	0.72	365	20	15	2.80	365	20	15	365	35	0.10
26	100	0.72	360	20	20	2.64	360	20	20	360	40	0.10

Under these conditions the process proceeded steadily as shown by the constant composition of the spent acid and nitroethylbenzene. The latter was obtained in the form of a light-yellow liquid, indicating that it did not contain tarry products. It did not contain ethylbenzene or dinitroethylbenzene. Hence we were able to recommend the elimination of steam distillation of nitroethylbenzene from the technological process. The nitroethylbenzene yield was 99.2-99.8% on the ethylbenzene taken for the reaction.

The spent acid also appeared as a clear, slightly yellow liquid, which contained 72-73% sulfuric acid, 0.5-1.5% nitric acid, 0.2-0.3% nitrogen oxides (calculated as nitrogen trioxide), and 0.03-0.15% nitro compounds. The sulfuric acid could be regenerated by denitration and subsequent concentration by known methods.

When ethylbenzene was nitrated with a nitrating mixture containing a nitric acid excess of less than 5% over that calculated for the ethylbenzene, the nitroethylbenzene formed contained unreacted ethylbenzene. The ethylbenzene content varied from 1.5 to 4.8% with a nitric acid excess of 1.0-3.5%.

An important feature of the present investigation was the development of a system of washing the acid nitroethylbenzene without discharging toxic wastes into the drainage. No investigations in this direction were carried out in the work published on ethylbenzene nitration.

In our experiments on continuous nitration of ethylbenzene, the nitroethylbenzene had an acidity of 0.61 to 1.16% after separation from the spent acid. It was established that the product could be freed from the acid by washing with water in three stages with a closed circulation system, removing wash water I, and adding it to the spent acid.

To develop a closed water-circulation system we carried out a cyclic experiment on the washing of nitroethylbenzene with water in three stages and 26 cycles of the wash water. The experimental procedure was as follows. Into a heated 0.75-liter separating funnel fitted with a stirrer were placed 100 g of nitroethylbenzene with an acidity of 0.72-1.16% and 380 ml of wash water I with 20 ml of wash water II. The mixture was stirred at 65-70° for 15 minutes, the stirrer stopped, and the separated nitroethylbenzene removed from the water. Of the so-called wash water I thus obtained, 20 ml was removed from the cycle, and 380 ml• used for the first washing of the next 100 g of nitroethylbenzene. After the first wash, the nitro product was washed a second time with 380 ml of wash water II with 20 ml of wash water III added, and then a third time with 380 ml of wash water III with 20 ml of fresh water added.

Thus, in the washing of nitroethylbenzene the modulus was taken as 4 with 20 ml of fresh water used for each 100 g of nitroethylbenzene and 20 ml of wash water I removed. The acidity of the wash water I removed from the cycle and the acidity of the washed nitroethylbenzene were determined after each wash. A total of 26 experiments with wash waters were carried out until the last 8-10 analyses of wash water I showed the same acidity and this was taken as indicating that the nitroethylbenzene washing system had been established.

The results of cyclic experiments on the washing of nitroethylbenzene with water are given in Table 2. The average acidity of the wash waters in a wash cycle after 26 circulations was as follows: 2.64% for wash water I, 0.26% for wash water II, and 0.038% for wash water III. As Table 2 shows, after 18 circulations of the wash water the washing process became stable at a nitroethylbenzene acidity of about 0.1% and a wash water I acidity of about 2.5-3%.

In order to reuse the sulfuric acid and eliminate the disposal of toxic waste water in the production of nitroethylbenzene, wash water I (200 kg per ton of nitroethylbenzene) may be added to the spent acid for regeneration. In this case the sulfuric acid content of the dilute spent acid would be 68-69%.

After three-stage washing with water in a closed water circulation system, the nitroethylbenzene was fractionated in vacuum without preliminary drying.

As the literature mentions washing of nitroethylbenzene with aqueous solutions of inorganic bases [3, 4], we also carried out experiments on the washing of nitroethylbenzene with aqueous sodium carbonate solution in the second wash. In this case the washing procedure was as follows: 50 ml of nitroethylbenzene with an acidity of 1.16% was washed at room temperature with 200 ml of water, then 200 ml of 5% aqueous sodium carbonate solution, and finally water again (twice with 200 ml portions). The acidity of the nitroethylbenzene washed in this way was 0.0175, 0.0125, 0.018 and 0.018% in the four experiments.

The fractionation of nitroethylbenzene, washed with water containing sodium carbonate and without it, was the same in each case and the quality of the o- and p-nitroethylbenzenes obtained was the same. On these grounds the sodium carbonate wash of nitroethylbenzene before its fractionation was eliminated.

EXPERIMENTAL

For the experiments we used ethylbenzene satisfying the requirements of VTU MKhP No. 3925-54. The nitrating mixtures were prepared from standard acids, "melange" and commercial sulfuric acid with the calculated amount of water added.

Continuous mononitration of ethylbenzene. Ethylbenzene was nitrated continuously to nitroethylbenzene in laboratory equipment consisting of two apparatuses, the main one and a buffer. Separation was carried out periodically in a separating funnel. The nitrators were glass apparatuses with 275 ml working capacity, connected at the top. The first nitrator (main one) was fitted with a stirrer, a reflux condenser, two graduated dropping funnels, and a thermometer. The second nitrator (buffer) was fitted with a stirrer, reflux condenser, and thermometer. The nitrators were cooled with tap water.

The main nitrator was charged with 114.6 g of ethylbenzene, and then over a period of 20 minutes, 160.5 g of nitrating mixture, containing 60.81% sulfuric acid, 23.16% nitric acid, and 16.03% water (F = 72.8%), was added

•To compensate for the evaporation of part of the water in the washing of nitroethylbenzene at 65-70°, enough fresh water was added in each experiment to make the amount up to 380 ml.

from the separating funnel with cooling and stirring. The temperature in the apparatus was kept within the range 40-45°. After the addition of the nitrating mixture, the temperature was kept at 50-55° for 30 minutes. Then the two components were added continuously at a rate of 19.1 ml of ethylbenzene and 26.75 ml of nitrating mixture in 5 minutes, which corresponded to the reaction mixture remaining in each reactor for 30 minutes. When the buffer apparatus was filled, the reaction mixture was collected in a separator and the nitroethylbenzene periodically separated from the spent acid and washed with water to an acidity of not more than 0.1%.

By continuous nitration of 2416 g of ethylbenzene with 6510 g of nitrating mixture of the above composition over a period of 11.2 hours, we obtained 3414 g of nitroethylbenzene (99.2% yield on ethylbenzene) of specific gravity 1.122, which did not contain ethylbenzene or dinitroethylbenzene. The amount of spent acid was 5480 g; its composition was as follows: 71.91% sulfuric acid, 0.28% nitric acid, 0.29% nitrogen oxides (calculated as nitrogen trioxide), and 0.02% nitro compounds.

Fraction distillation of the nitroethylbenzene on a column 1500 mm high, which we described previously [5], yielded 38-40% p-nitroethylbenzene, 40-42% o-nitroethylbenzene, 18.22% of an intermediate fraction (containing o-, m-, and p-nitroethylbenzenes), and 1.5-3% distillation residue.

SUMMARY

1. A continuous method was developed for the nitration of ethylbenzene to nitroethylbenzene with a nitrating mixture of nitric and sulfuric acids.

2. A method was developed for washing the acid nitroethylbenzene with a closed water circuit without the disposal of toxic waste water into the drainage.

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NITRO DERIVATIVES OF ACENAPHTHENE

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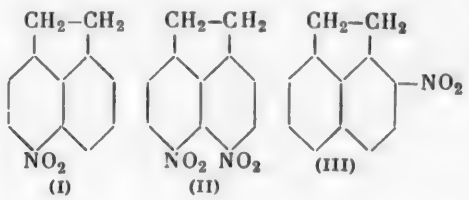
In recent years nitro derivatives of acenaphthene have attracted attention as interesting and extremely accessible intermediates in the synthesis of various dyes and some other compounds.

Meanwhile, the method of preparing them has remained the same as described in the last century.

Quincke obtained 4-nitro- and 4,5-dinitroacenaphthene by the action of fuming nitric acid on a solution of acenaphthene in glacial acetic acid [1, 2].

Graebe and Brions nitrated acenaphthene under the same conditions with nitric acid with sp.g. 1.47-1.48. The yield of 4-nitroacenaphthene was 90% of theoretical [3].

Sachs and Mosebach proposed the nitration of acenaphthene with concentrated nitric acid. They obtained 4-nitroacenaphthene (I) in a yield of 84% of theoretical [4]. If acenaphthene was nitrated with twice the amount of concentrated nitric acid, 4, 5-dinitroacenaphthene (II) was obtained in 40% yield.



A mononitroacenaphthene with m.p. 155° was described by Jandrier [5] but later investigators could not obtain it [3, 4]. Jandrier nitrated acenaphthene with nitric acid with sp.g. 1.34.

Monti and his co-workers studied the nitration of acenaphthene and other aromatic hydrocarbons with a solution of nitrous fumes in ether or acetic acid [6-8]. Of the hydrocarbons they studied, acenaphthene was found to be the most reactive. Acenaphthene is nitrated by liquid N_2O_4 to 4, 5-dinitroacenaphthene even at - 15°. In an attempt at electrochemical nitration of acenaphthene, it was observed that with this hydrocarbon, in contrast to naphthalene, there was extensive oxidation, with strong gas evolution [9].

Morgan and Harrison [10] established that if acenaphthene is nitrated in acetic anhydride solution, then together with 4-nitroacenaphthene (I), a considerable amount of 2-nitroacenaphthene (III) is formed.

Krivonos developed a method of nitrating acenaphthene with weak nitric acid without solvent [11].

Despite the attractiveness of this method, according to our investigations, under the conditions adopted by Krivonos the yield of 4-nitroacenaphthene does not exceed 60%.

The nitration of acenaphthene has been studied by Japanese chemists since the war [12, 13].

Acenaphthene was converted to the dinitro derivative in glacial acetic acid with 98% nitric acid (9 moles of acid to 1 mole of acenaphthene).

The yield of 4, 5-dinitroacenaphthene with m.p. 210-211.5° was 48.5% of theoretical.

Under these conditions, 2, 4- and 2, x-dinitroacenaphthene were formed simultaneously and these were separated by boiling the nitration product with benzene [13].

In the nitration of acenaphthene by other methods, other isomers are also apparently formed together with 4-nitro- and 4, 5-dinitroacenaphthene, but there is no satisfactory method of separating them as yet. Their structures have also been studied insufficiently.

Up to the present time, 4-nitroacenaphthene used in technology has been obtained by nitration of acenaphthene in acetic acid. Although this method gives a good product in a yield of 90% and above, it suffers from essential drawbacks. A large amount of glacial acetic acid is consumed,and it is practically impossible to regenerate it. Then, under production conditions, glacial acetic acid is a very aggressive agent and its vapor penetrates through leaks in the apparatus, creating unbearable conditions in the plant.

We found that acenaphthene is very readily nitrated in dichloroethane solution. We studied the action of nitric acid of various concentrations on acenaphthene in this solvent. In dichloroethane, acenaphthene is nitrated even by 7% nitric acid, though very slowly.

If acenaphthene is nitrated wtih 50% nitric acid and stronger, together with the mono derivative, a certain amount of dinitroacenaphthene and their oxidation products are formed.

By the method we developed, acenaphthene in dichloroethane is nitrated quantitatively to 4-nitroacenaphthene by nitric acid of sp.g. 1.3.

If acenaphthene in dichloroethane is nitrated with nitric acid of sp.g. 1.45, 4. 5-dinitroacenaphthene is obtained in a yield of 60-65%.

In dichloroethane solution, acenaphthene is nitrated at 15-20° by weaker nitric acid than is required for nitration in acetic acid.

Under these conditions the reaction mixture has to be cooled as witha rise in temperature (from the heat of reaction), in addition to nitration, oxidation begins with the liberation of nitrogen oxides.

The nitration to dinitroacenaphthene proceeds with somewhat more difficulty. It is advantageous to nitrate acenaphthene to mononitroacenaphthene with nitric acid of sp.g. 1.3-1.4 first and then use a nitrating mixture consisting of equal parts of nitric acid of sp.g. 1.45 and concentrated sulfuric acid.

EXPERIMENTAL

4-Nitroacenaphthene. In the nitration of acenaphthene in acetic acid, we obtained the best results under the following conditions: 25 g of acenaphthene and 150 ml of glacial acetic acid were heated on a water bath until solution was complete. The solution was then cooled to 20°, and then,ignoring the acenaphthene crystals precipitating from the solution, we added 25 ml of nitric acid (sp.g. 1.37) dropwise over a period of 30 minutes. All the acenaphthene gradually dissolved and then nitroacenaphthene began to precipitate from the solution.

A brief heating on a water bath gave a clear solution which was left until the following day. The precipitated 4-nitroacenaphthene was collected and washed twice with a small amount of 80% acetic acid. We obtained 26.5-28 g of 4-nitroacenaphthene, representing 82-88% of the theoretical yield. The product had m.p. 101-102°. Dilution of the filtrate with water yielded a further 4-6 g of a low-melting product.

As this method is unsuitable in technology due to the large consumption of acetic acid, which is practically impossible to regenerate, we studied the possibility of nitrating acenaphthene in other, more readily accessible solvents or without them.

We found that nitration without solvent did not proceed to completion since the nitroacenaphthene formed coated the as yet unreacted acenaphthene and hindered its nitration. The yield did not exceed 60% of theoretical.

There is the possibility that the yield could be increased if an apparatus were constructed in which, together with efficient stirring, the reaction product was also ground. As yet this method is unsuitable due to the low yield and impure nature of the product obtained.

TABLE 1

Nitration of Acenaphthene in Dichloroethane to 4-Nitroacenaphthene. Acenaphthene 10 g, Dichloroethane 20 ml, t = 10-15°, duration of an experiment 1 hr 30 min

Expt. No.	Specific gravity of nitric acid	Nitric acid concentration (%)	Amount of nitric acid (in ml)	Nitroacenaphthene (in g)	Melting point (in °C)
1	1.042	7.7	100	10.2	low-melting
2	1.110	18.5	40	11.1	low-melting
3	1.255	40.58	32	12.95	93—99
4	1.270	42.87	15	12.7	50—70
5	1.270	42.87	30	12.8	92—99
6	1.30	47.5	10	12.7	86—96
7			12	12.85	93—99
8			12	12.85	92—99
9			12	12.9	93—98
10			13	12.8	90—98
11			13	12.9	93—99
12			14	12.85	87—97
13			15	12.85	85—99
14	1.370	59.39	12	12.85	83—93
15	Mixture	47.9	7	12.1	60—83
16			8	12.5	66—83
17			9	12.75	85—92
18			10	12.8	92—96
19			10	12.85	93—98
20			11	12.85	83—95
21			12	12.9	80—93

Good results were obtained by using organic solvents which are immiscible with water.

Of the solvents tested (dichloroethane, benzene, nitrobenzene, and chlorobenzene) the most suitable was found to be dichloroethane.

Nitration in dichloroethane. A mixture of 10 g of acenaphthene and 20 ml of dichloroethane was stirred and cooled with tap water (10-15°) and 12 ml of nitric acid with sp.g. 1.3 added dropwise over a period of 25 minutes.

After addition of the acid, the mixture was stirred for a further one hour, washed several times with water to remove excess nitric acid, the dichloroethane steam distilled, and the residue dried to constant weight at 60-70°. We obtained 12.8-12.9 g of 4-nitroacenaphthene with m.p. 92-99° (theoretical yield 12.92 g). This product was pure enough for technical requirements.

If a product with a higher melting point was required, the crude acenaphthene (12.8-12.9 g) was recrystallized from 70 ml of 85% acetic acid. We obtained 11.9-12.2 g of 4-nitroacenaphthene with m.p. 99-102°.

The same results were obtained if 10 g of acenaphthene was nitrated in dichloroethane solution with 10 ml of a mixture containing 47.5% nitric acid, 4.47% sulfuric acid, and 48.03% water.

Nitration in chlorobenzene solution gave a product of poorer quality and when benzene was used as solvent, some of it was nitrated together with the acenaphthene, though only a very small amount.

We carried out several series of experiments to study the nitration of acenaphthene in dichloroethane with nitirc acid of various concentrations.

Table 1 gives data from some of these experiments, showing the effect of various factors on the yield and quality of the 4-nitroacenaphthene. As Table 1 shows, acenaphthene is nitrated by 8% nitric acid. We could not make an unequivocal choice of the optimal conditions (experiments No. 7-9, 3 and 5).

TABLE 2

Nitration of Acenaphthene to 4, 5-Dinitroacenaphthene. In Each Experiment 10 g of Acenaphthene and 30 ml of Dichloroethane were used; t = 15-20°

Expt. No.	HNO_3 taken (in ml)				H_2SO_4 taken (in ml)	Duration of expt.* (in hr)	Nitro product obtained (in g)	Melting point (in °C)
	I		II					
	specific gravity	amount	specific gravity	amount				
1		6	1.51	10	—	1	10.2	187—198
2		8	1.51	10	—	1	10.0	192—200
3		8	1.51	12	—	2	10.3	184—198
4		8	1.51	12	—	1.5	10.5	188—195
5		8	1.51	16	—	1	10.2	177—198
6		10	1.51	10	—	1	11.5	200—205
7		8	1.365	3	6	1	7.1	191—204
8	1.365	8	1.30	6	20	3	11.1	186—198
9		8	1.30	10	25	1	12.0	180—201
10		7	1.30	10	25	1	10.9	195—205
11		8	1.11	15	30	1	11.1	190—203
12		8	1.23	10	15	1	10.8	180—195
13		10	1.23	5	10	1	10.7	178—196
14		10	1.23	10	20	1	11.9	196—205
15		10	1.23	10	20	1	11.4	200—205
16	1.4	10	1.4	10	10	2	11.4	196—198
17	1.4	8	1.4	8	8	2	10.6	192—200
18	1.345	12	1.345	12	10	2	11.3	195—197

*The time for which the reaction mixture was stirred after addition of the acid is given.

The best results were obtained with nitric acid whose initial concentration must be less than 50% and final one, not less than 25%. This made it necessary to work with a definite excess of nitric acid. In work with the mixture, the excess of nitric acid could be reduced considerably (experiments 18 and 19).

4, 5-Dinitroacenaphthene. Nitration to dinitroacenaphthene also proceeds in dichloroethane solution. The reaction proceeds less vigorously than to the mononitro derivative and only with more concentrated nitric acid or nitrating mixture.

In experiments No. 15-21 the nitration was performed with a mixture consisting of 47.5% nitric acid, 4.47% sulfuric acid, and 48.03% water.

As concentrated nitric acid causes tar formation as well as nitration of the acenaphthene, it was better to nitrate the acenaphthene to mononitroacenaphthene with weaker nitric acid first and then continue the reaction with stronger nitric acid.

We developed several variants for synthesizing 4, 5-dinitroacenaphthene in 80-85% yield on the dinitro product content of the nitrated mass. The pure product could be isolated in a yield of about 65%.

Variant 1. To 10 g of acenaphthene was added 30 ml of dichloroethane and with cooling with tap-water (10-15°) and stirring, 10 ml of nitric acid of sp.g. 1.365 was added dropwise over a period of 10 minutes. After 5 minutes a further 10 ml of fuming nitric acid (sp.g. 1.51) was added dropwise and stirring continued for 1 hour. After 20-30 minutes from the beginning of the reaction, crystals of dinitroacenaphthene began to separate from the solution. The mixture was left overnight. On the following day the acid layer was decanted from the precipitated nitro product, which was washed with water, the dichloroethane sucked off on a Buchner funnel, and the residue washed three times with 5 ml portions of dichloroethane and again with water. We obtained 10.8-11.5 g of 4, 5-dinitroacenaphthene in the form of beautiful golden-yellow needles (68.1-72.6%); the melting point of the product was 200-205°.

Variant 2. Over a period of 20 minutes, an acid mixture of 40 ml of nitric acid (sp.g. 1.365), 20 ml of concentrated sulfuric acid, and 20 ml of water was added dropwise to 10 g of acenaphthene and 30 ml of dichloroethane. The mixture was stirred for 2 hours and then left until the following day. Subsequent treatment was as in variant 1. We obtained 10.7 g of dinitroacenaphthene.

Distillation of the dichloroethane from the nitro product after it had been washed free from acid gave 13.5-14.5 g of crude nitro product from 10 g of acenaphthene. For purification, the nitro product was treated with a 10-fold amount of hot toluene in which dinitroacenaphthene is difficultly soluble. After this treatment the product melted at about 215°.

Table 2 gives data on some of the experiments on the nitration of acenaphthene to 4, 5-dinitroacenaphthene.

In all the experiments described, to a solution of acenaphthene in dichloroethane a weaker solution of nitric acid was first added with cooling to prepare the mononitro product and then after a few minutes more concentrated nitric acid or a nitrating mixture was added, usually without cooling. The precipitated dinitroacenaphthene was collected on a Buchner funnel and washed three times with dichloroethane (5 ml portions) and then with water. The nitro product was dried at 100-110°.

The nitration proceeded more vigorously in the presence of sulfuric acid, but concentrated sulfuric acid produced partial oxidation and tar formation.

We obtained a good yield of the dinitro product only with a large excess of nitric acid.

SUMMARY

1. In a study of the nitration of acenaphthene in various solvents with nitric acid and nitrating mixture of various concentrations, it was shown that of all the solvents investigated (acetic acid, nitrobenzene, benzene, dichloroethane, and chlorobenzene) dichloroethane gave the best results.

2. The method developed for nitration of acenaphthene made it possible to obtain 4-nitroacenaphthene and 4, 5-dinitroacenaphthene in high yields.

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HYDROLYSIS KINETICS OF SULFONIC ACIDS OF XYLENE ISOMERS AND ETHYLBENZENE IN SULFURIC ACID

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One of the methods of isolating individual isomers from technical xylene is sulfonation with subsequent hydrolysis of the sulfonic acids obtained:

$$(CH_3)_2C_6H_3SO_3H + H_2O \longrightarrow (CH_3)_2C_6H_4 + H_2SO_4.$$

The hydrolysis is accelerated in the presence of mineral acids. The reaction proceeds at an appreciable rate at temperatures above 100°.

The literature contains a description of the preparative production of m-xylene by hydrolysis of its sulfonic acid [1-13]. Kizhner and his co-workers [6, 14, 15] found temperature conditions for hydrolyzing o-, m-, and p-xylenesulfonic acids. This work was of a qualitative character and gave no information on the kinetics of the process. The hydrolysis kinetics of m- and p-xylenesulfonic acids in the presence of hydrochloric acid at different concentrations and of m-xylenesulfonic acid in the presence of 50 and 75% sulfuric acid at 100° were studied by Crafts [16, 17]. In this work it was shown that raising the mineral acid concentration increased the hydrolysis rate. By using large excesses of mineral acid and water, Crafts was able to describe the kinetic data by the equation of a reaction of the first order [16, 18].

We undertook a detailed study of the kinetics of the hydrolysis of sulfonic acids of xylene isomers and ethylbenzene in the presence of sulfuric acid at various concentrations as the compounds are hydrolyzed in the presence of sulfuric acid in practice.

EXPERIMENTAL

Preparation of sulfonic acids. The sulfonic acids were prepared from appropriate pure hydrocarbons by sulfonation. To 300 ml of hydrocarbon was added 360 ml of concentrated sulfuric acid dropwise with vigorous stirring at about 40°. After the addition of the acid, the temperature was raised to 90-95° and kept there for 40 min in the case of m- and o-xylenes and for 2 hr in the case of p-xylene and ethylbenzene. The reaction mixture was then cooled, separated from unreacted hydrocarbon where necessary, and poured into half its volume of ice water. After dilution, the mixture was cooled to 0-5°. The precipitated sulfonic acid was collected and recrystallized twice from water (1/5 of the weight of the sulfonic acid) and then once or twice from chloroform. After separation from the chloroform, the sulfonic acid was dried in a stream of dry air to remove residual solvent. The sulfonic acids obtained in this way contained 2 moles of water of crystallization per mole of sulfonic acid.

Under the sulfonation conditions described, o- and m-xylene and ethylbenzene gave one sulfonic acid each with the sulfonyl group in position 4 [16, 19, 20]; p-xylene gives the only possible sulfonic acid.

Experimental procedure. Into a flask fitted with a thermometer and a multibulb reflux condenser, cooled with ice water, was placed a weighed sample of sulfonic acid (about 10 g) and a definite amount of sulfuric acid of a given concentration. The amount of sulfuric acid taken was such that for each mole of sulfonic acid there

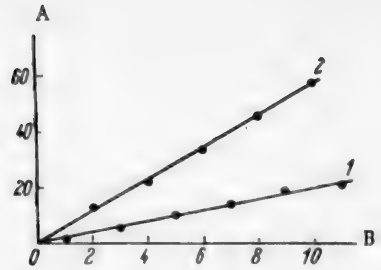

Fig. 1. Hydrolysis of m-xylenesulfonic acid in 50% sulfuric acid. A) Degree of hydrolysis (in %); B) time (in hr). Temperature (in °C): 1) 100, 2) 115.

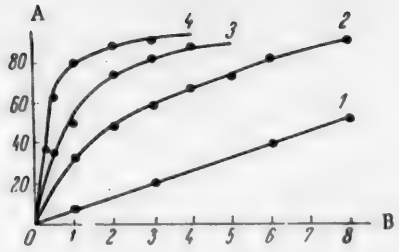

Fig. 2. Hydrolysis of m-xylenesulfonic acid in 60% sulfuric acid. A) Degree of hydrolysis (in %); B) time (in hr). Temperature (in °C): 1) 100, 2)115, 3)130, 4) 140.

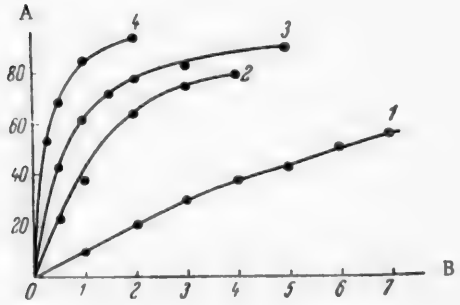

Fig. 3. Hydrolysis of m-xylenesulfonic acid in 65% sulfuric acid. A) Degree of hydrolysis (in %); B) time (in hr). Temperature (in °C): 1) 100, 2) 115, 3) 130, 4) 140.

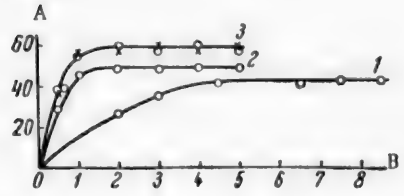

Fig. 4. Hydrolysis of m-xylenesulfonic acid in 70% sulfuric acid. A) Degree of hydrolysis (in %); B) time (in hr). Temperature (in °C): 1) 100, 2) 115, 3) 130 and 140.

was 70-75 moles of water, contained in the sulfuric acid. This made it possible to keep the medium at practically constant acidity during the experiment.

Under these conditions all the sulfonic acids of the xylene isomers and ethylbenzene dissolved completely at the experimental temperatures.

The apparatus was placed in a thermostatted glycerol or oil bath, previously heated to the given temperature. The time was measured from when the temperature of the liquid in the flask reached this value (usually 10-15 min after immersion). After being heated for a definite time, the apparatus was withdrawn from the bath, rapidly cooled, its contents treated with water and transferred to a burette, where the amount of hydrocarbon liberated was measured. The amount of sulfonic acid decomposed was calculated from the amount of hydrocarbon.

The results of experiments on the hydrolysis of m- and p-xylene-sulfonic acids are presented graphically (Figs. 1-8). As the hydrolysis of other sulfonic acids proceeded quite analogously, graphs showing the course of their hydrolysis are not given to save space.

In sulfuric acid at concentrations of 50-65% (Figs. 1-3, 6, and 7), the hydrolysis slowed as the reaction proceeded but no equilibrium state was observed.

In the hydrolysis of m- and p-xylenesulfonic acid in sulfuric acid with concentrations of 70 and 75% (Figs. 4, 5, and 8), the reaction first proceeded and then an equilibrium was established between the hydrolysis of sulfonic acid and the sulfonation of hydrocarbon. This was especially characteristic of 75% sulfuric acid where the hydrolysis rate and the establishment of equilibrium depended on whether there was stirring or not. With stirring, equilibrium was established at 90 and 100° at a hydrolysis degree of about 4% and at 115 and 130°, at a hydrolysis degree of about 6% (Fig. 5). When the hydrolysis was carried out without stirring, no equilibrium was observed at a hydrolysis degree of 25%.

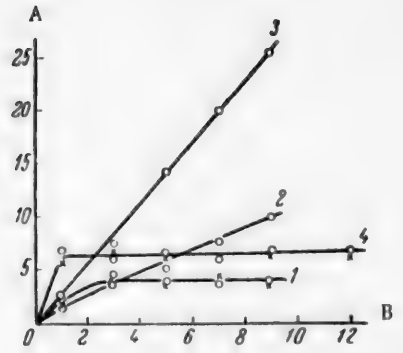

Fig. 5. Hydrolysis of m-xylenesulfonic acid in 75% sulfuric acid. A) Degree of hydrolysis (in %); B) time (in hr). Temperature (in °C): 1) 90 and 100 (with stirring); 2) 90 (without stirring); 3) 100 (without stirring); 4) 115 and 130 (without stirring).

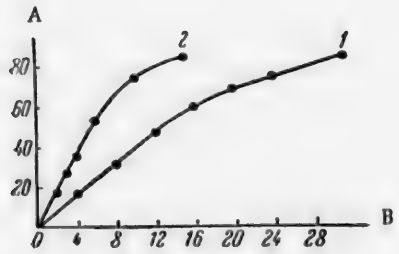

Fig. 6. Hydrolysis of p-xylenesulfonic acid in 60% sulfuric acid. A) Degree of hydrolysis (in %); B) time (in hr). Temperature (in °C): 1) 130, 2) 140.

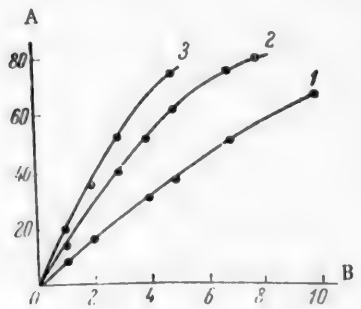

Fig. 7. Hydrolysis of p-xylenesulfonic acid in 65% sulfuric acid. A) Degree of hydrolysis (in %); B) time (in hr). Temperature (in °C): 1) 130, 2) 140, 3) 145.

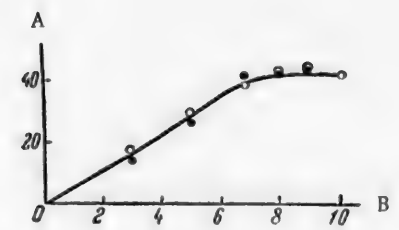

Fig. 8. Hydrolysis of p-xylenesulfonic acid in 70% sulfuric acid at 130 and 140°. A) Degree of hydrolysis (in %) B) time (in hr).

These facts may be explained if it is considered that the rate of sulfonation increases with stirring while the rate of hydrolysis, as a homogeneous reaction, is independent of stirring. Therefore, in the absence of stirring, the rate of hydrolysis is greater than the rate of sulfonation and equilibrium is not produced, while with stirring, the rate of sulfonation increases and becomes equal to the rate of hydrolysis, i.e., equilibrium is established.

From the data obtained we calculated the rate constant of the hydrolysis reaction k from the equation for a reaction of the first order:

$$k = \frac{2.303}{t} \lg \frac{a}{a - x} \text{ [1/min]}$$

where t is the time (in min), a the initial amount of sulfonic acid, and x the amount of sulfonic acid decomposed at moment of time t.

By applying this equation to the experimental data obtained at 100 and 115°, it was shown that the rate constant was constant with time for all sulfuric acid concentrations. For the hydrolysis of m-xylenesulfonic acid in 60 and 65% sulfuric acid at 130 and 140° there was a decrease in the reaction rate constant with time. Under these conditions the reverse reaction of sulfonation of the m-xylene formed apparently began to have an effect and this was reflected in the experimental hydrolysis constant. Therefore,

Hydrolysis Rate Constants of Sulfonic Acids of Xylene Isomers and Ethylbenzene, $k \cdot 10^4$ 1/min

Temperature (°C)	Hydrolysis rate constants																			
	m-xylenesulfonic acid					p-xylenesulfonic acid				o-xylenesulfonic acid				ethylbenzenesulfonic acid						
	sulfuric acid concentration (in wt. %)																			
	50	60	65	70	75	60	65	70	60	65	70	60	65	70	60	65	70	60	65	70
90	—	—	—	—	2.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
100	3.56*	12.6	21.4	26.2	4.8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
115	13.6*	48.5	67.5	90.0	10.7	—	—	—	—	—	—	—	—	—	0.59*	1.47	—	—	—	—
130	—	148	186	145	10.3*	8.8*	15.3	10.4*	—	—	—	—	—	—	2.47*	3.37	0.74*	—	—	—
140	—	312	362	149*	—	21.4*	29.8	10.4*	3.56*	1.60*	—	—	—	—	—	5.35	0.96*	—	—	—
145	—	—	—	—	—	—	40.5	—	—	—	—	—	—	—	—	—	—	—	—	—
Coefficient A of Arrhenius equation	12.219	10.995	10.014	9.750**	7.202***	12.827	6.133	—	—	—	—	Hydrolysis proceeded at an insignific-antly low rate.			—	11.693	5.052			
Coefficient B of Arrhenius equation	5857	5178	4736	4600**	3945***	6400	3583	—	—	—	—				—	6259	3800			
Activation energy (kcal/mole)	26.8	23.7	21.7	21.0**	18.1***	29.2	16.4	—	—	—	—				—	28.6	17.8			

*Rate constants calculated directly from kinetic data.

**Over the temperature range 100-130°.

***Over the temperature range 90-115°.

to calculate the hydrolysis constants of m-xylenesulfonic acid at 130 and 140° in 60 and 65% sulfuric acid, we used only the initial sections of the hydrolysis curves, where the reverse reaction of sulfonation had no effect.

In hydrolysis experiments which ended in the establishment of equilibrium (m- and p-xylenesulfonic acids in 70 and 75% sulfuric acid), we also used rate constants calculated from the initial sections of the curves.

Experiments showed that the change in the hydrolysis rate constant of sulfonic acids with temperature obeyed the Arrhenius equation $\lg k = A - \frac{B}{T}$, with the exception of the regions where equilibrium with the reverse reaction of sulfonation was established.

The table gives the values of the hydrolysis rate constants for sulfonic acids of xylene isomers and ethylbenzene, corrected according to the Arrhenius equation, and also the coefficients of the Arrhenius equation and the activation energies.

The table shows that the maximum rate of hydrolysis of sulfonic acids of m- and p-xylenes and ethylbenzene are achieved at a sulfuric acid concentration of 65% (at temperatures of 130-140°), but in the lower temperature region (100-130°) the maximum hydrolysis rate is observed in 70% sulfuric acid (before equilibrium is established). In the case of o-xylenesulfonic acid, the maximum of the hydrolysis rate is apparently displaced into a region of lower sulfuric acid concentrations (about 60%).

Attention is attracted by the fact that in the region of sulfuric acid concentrations of 65-70%, together with the maximum rate of hydrolysis of sulfonic acids, an increase is observed in the solubility of sulfonic acids, which is connected with the formation of the ion $ArSO_3H_2^+$ [21]. In our opinion this confirms the point of view of Spryskov [22] on the mechanism of sulfonic acid hydrolysis, according to which the first stage of the hydrolysis reaction is the addition of a hydroxonium ion to the sulfonic acid molecule:

$$ArSO_3H + H_3O^+ \rightleftarrows (ArSO_3H \ldots . H_3O)^+.$$

In the second stage, the $-SO_3H$ group is eliminated from the intermediate complex by the reaction

$$(ArSO_3H \ldots . H_3O)^+ + HSO_4^- \longrightarrow ArH + 2H_2SO_4.$$

Both stages of the reaction are accelerated by an increase in the mineral acid concentration.

The decrease in the hydrolysis rate with an increase in sulfuric acid concentration from 70 to 75% and above is explained by the reverse reaction of xylene sulfonation, which occurs under these conditions [24].

SUMMARY

1. By studying the hydrolysis kinetics of sulfonic acids of xylene isomers and ethylbenzene in the presence of sulfuric acid at various concentrations, it was shown that the hydrolysis rates of sulfonic acids of m- and p-xylenes and ethylbenzene have maxima in the sulfuric concentration range of 65-70%, while the hydrolysis rate of o-xylenesulfonic acid is maximum at a sulfuric acid concentration of about 60%.

2. The hydrolysis rate of the sulfonic acids decreases in the following order: m-xylenesulfonic acid > > p-xylenesulfonic acid > ethylbenzenesulfonic acid ≤ o-xylenesulfonic acid.

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LIQUID-PHASE HYDRATION OF ISOBUTYLENE IN THE PRESENCE OF SULFURIC ACID

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In recent time there has been extensive development of the synthesis of a number of alcohols from appropriate gaseous, unsaturated hydrocarbons (C_2H_4, C_3H_6, n-C_4H_8, and iso-C_4H_8), present in the gases from the cracking and pyrolysis of petroleum, by reacting them with sulfuric acid in the gas or the liquid phase and subsequently hydrolyzing the reaction product with water.

The purpose of the present work was to investigate the reaction of liquefied isobutylene with sulfuric acid at various concentrations (from 41 to 61%) and determine whether direct hydration occurs in this stage.

Butlerov [1] showed that liquefied isobutylene is gradually hydrated in the presence of dilute sulfuric acid to form tertiary isobutyl alcohol.

According to contemporary ideas [2], in the hydration of unsaturated hydrocarbons in the presence of dilute acid, there is first the addition of a proton to the molecule hydrated to form a carbonium ion (R^+), which is then hydrated:

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- + H_3O^+ \rightleftarrows -\overset{|}{\underset{|}{\underset{H}{C}}}-\overset{|}{\underset{|}{C}}- + H_2O,$$

$$R^+ + H_2O \rightleftarrows ROH_2^+.$$

Subsequent reaction of the hydrated carbonium ion with a second water molecule forms an alcohol molecule and an oxonium ion:

$$ROH_2^+ + H_2O \rightleftarrows ROH + H_3O^+$$

The reaction of isobutylene with more concentrated sulfuric acid forms isobutylsulfuric acid and hydrolysis of this yields tertiary isobutyl alcohol:

$$C_4H_8 + H_2SO_4 \rightleftarrows C_4H_9OSO_2OH,$$

$$C_4H_9OSO_2OH + H_2O \rightleftarrows C_4H_9OH + H_2O.$$

In the reaction of isobutylene with very dilute sulfuric acid, the hydrocarbon is hydrated directly to form tertiary isobutyl alcohol and with more concentrated acid it forms isobutylsulfuric acid. When sulfuric acid of average concentration is used, there is apparently the parallel formation of isobutylsulfuric acid and the direct hydration of isobutylene. As one of us previously found [3], even with 40% sulfuric acid there is some direct hydration of isobutylene, while with 65% acid, isobutylsulfuric acid is formed [4].

TABLE 1

Density (d_4^{20}) and Specific Electrical Conductivity (κ) of Reaction Products

Original sulfuric acid concentration								
41.27%			51.39%			61.25%		
C_4H_8 absorbed (m/m of H_2SO_4)	d_4^{20}	$\kappa \cdot 10^3$, $\Omega^{-1} \cdot cm^{-1}$	C_4H_8 absorbed (m/m of H_2SO_4)	d_4^{20}	$\kappa \cdot 10^3$, $\Omega^{-1} \cdot cm^{-1}$	C_4H_8 absorbed (m/m of H_2SO_4)	d_4^{20}	$\kappa \cdot 10^3$, $\Omega^{-1} \cdot cm^{-1}$
0.0	1.314	66.0	0.0	1.408	51.9	0.0	1.511	34.0
0.60	1.205	27.9	0.67	1.246	15.7	0.24	1.404	17.4
1.00	1.148	16.6	1.01	1.179	—	0.46	1.343	—
1.20	1.127	12.8	1.25	1.137	6.1	0.60	1.303	7.3
2.25	1.039	2.2	1.65	1.099	3.2	0.65	1.291	6.3
4.10	0.965	0.9	2.13	1.042	1.3	(0.83)	1.232	4.4
5.58	0.919	—	(3.1)	0.984	0.3	1.07	1.215	2.7
5.6	0.913	0.5	4.33	0.937	0.1	1.11	1.199	—
5.90	0.910	0.3	4.62	0.917	—	2.09	1.090	0.4
6.70	0.904	0.3	—	—	—	3.59	0.988	0.1
6.80	0.899	—	—	—	—	4.26	0.974	—
7.40	0.877	0.1	—	—	—	4.35	0.969	0.1
—	—	—	—	—	—	4.51	0.964	0.04

Consequently, among the reaction products of liquefied isobutylene and sulfuric acid at different concentrations, one might expect the presence of both isobutylsulfuric acid and also tertiary isobutyl alcohol. The reaction products may also contain a certain amount of isobutylene polymers, especially with more concentrated acid (65-70%). The formation of the neutral ester diisobutyl sulfate by the addition of two molecules of isobutylene to sulfuric acid is improbable, so that this process is excluded.

The complex composition of the reaction products should have a considerable effect on its density and electrical conductivity. Isobutylsulfuric acid is an ester of sulfuric acid which dissociates comparatively little and should therefore have a lower electrical conductivity than the original acid. The formation of the tertiary alcohol should lower the electrical conductivity of the reaction product even more. Therefore, the main investigation methods used in the present work were determination of the density and electrical conductivity of the reaction products.*

EXPERIMENTAL

Working procedure. For the work we used isobutylene obtained by dehydration of pure tertiary isobutyl alcohol (m.p. 25°) over sulfuric acid [3].

Experiments on the absorption of isobutylene by sulfuric acid were carried out in thick-walled tubes, which were first charged with sulfuric acid (1-5 ml) with the concentrations 41.27, 51.39, and 61.25% and then cooled in solid carbon dioxide and a calculated amount of liquid isobutylene added. The sealed tubes were shaken at room temperature for 2 to 5 hours until the isobutylene dissolved completely and a homogeneous solution was formed.

At the end of the reaction, the unreacted, dissolved isobutylene was evaporated, and then the density and electrical conductivity of the reaction product determined.

In the absence of traces of polymerization, the degree of saturation of the sulfuric acid by isobutylene was determined by the increase in weight of the acid and by titration of the water-diluted reaction product with 0.1 N aqueous alkali solution. In addition, the degree of saturation of the acid was determined by distillation of aqueous alcohol from the water-diluted (1:2 by volume) reaction product. The amount of alcohol formed was determined from the density of the alcohol distillate [5].

*V. M. Trofimov participated in the work.

The electrical conductivity of the starting sulfuric acid and the reaction product was determined by the usual method with a compensation bridge circuit [6]. The bridge was fed from a sonic frequency (~1500 cps) transitron value generator at a potential of 3 v. The determination was made in a glass tube (internal diameter 1.5 cm), in which were fixed a pair of platinized platinum electrodes, made from wire 0.5 mm in diameter and 1.5 cm long and sealed into a narrow glass tube (5-6 mm in diameter). The distance between the electrodes was 10 and 14 cm, depending on the electrical conductivity of the reaction product.

Electrical Conductivity of the Reaction Product

Investigation showed that the specific electrical conductivity of the reaction product decreased sharply as isobutylene was absorbed (Table 1, Fig. 1). The reaction products from 41.27% acid had a higher electrical conductivity than those from 51.39 and 61.25% acid. No breaks or inflections were observed on the curves characterizing the specific electrical conductivity, indicating that the process was of a similar nature during its whole course.

It should be noted that at all the sulfuric acid concentrations studied, there was a considerable degree of reaction, corresponding to the absorption of more than one mole of isobutylene per mole of acid. This indicates the presence of direct hydration and not only in the case of 41.27% sulfuric acid, which we reported previously [3], but also when more concentrated acid was used (61.25%).

Density of Reaction Products

It was found (Table 1, Figs. 2-4, curves 2) that the density of the reaction products, like the electrical conductivity, fell uniformly with the extent of the process. This indicates a certain uniformity of the process during its whole course.

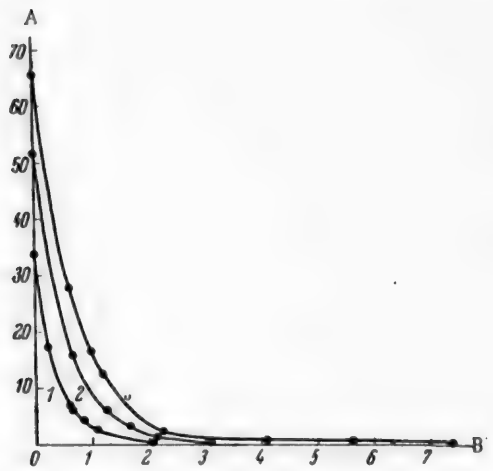

Fig. 1. Relation of specific electrical conductivity $\kappa \cdot 10^2$ ($\Omega^{-1} \cdot cm^{-1}$) of the reaction products (A) to the amount of isobutylene absorbed by one mole of sulfuric acid (B). Reaction products obtained with the following sulfuric acid concentrations (in %): 1) 61.25, 2) 51.39, 3) 41.27.

From the data obtained on the density it was possible to calculate the volume of the reaction products and compare it with the original volume of sulfuric acid. As the acid was saturated with isobutylene, the volume of the reaction products increased to a considerable extent. The volume of the reaction products relative to the volume of the initial acid was directly proportional to the amount of isobutylene absorbed (Fig. 5) and the more concentrated the starting sulfuric acid, the stronger was the increase in the volume of the reaction products. It should be remembered that the composition of the reaction products changed quite strongly with the depth of the process. Thus, in the initial stage of the reaction, when less than one mole of isobutylene was absorbed per mole of sulfuric acid, isobutylsulfuric acid was formed and with a higher degree of saturation of the sulfuric acid there was also direct hydration of the isobutylene. Consequently, in this stage there was present not only isobutylsulfuric acid and possibly free sulfuric acid, but also tertiary isobutyl alcohol, the amount of which must have gradually increased. Due to the latter direction of the reaction, the amount of free water present in the system must have gradually decreased as water is consumed in the hydration of isobutylene. The fact that with a considerable change in the composition of the reaction products, the dependence of their volume relative to one volume of original acid was expressed by a straight line indicates that the process was definitely uniform in all of its stages.

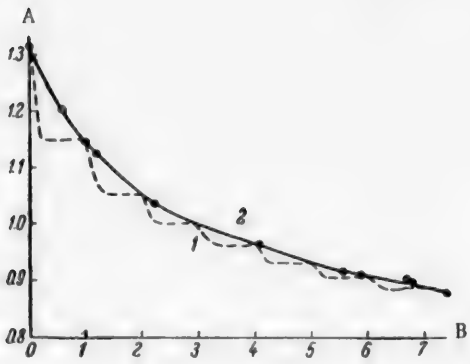

Fig. 2. Relation of the density of the reaction product (d_4^{20}), obtained with 41.27% sulfuric acid, (A) to the number of moles of isobutylene absorbed per mole of acid (B). 1) Calculated by the rule of additivity; 2) experimental data.

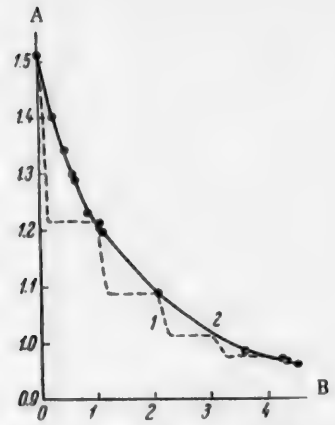

Fig. 3. Relation of the density of the reaction product (d_4^{20}), obtained with 51.39% sulfuric acid, (A) to the number of moles of isobutylene absorbed per mole of acid (B). 1) Calculated by the rule of additivity; 2) experimental data.

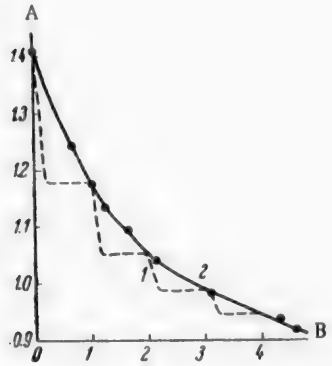

Fig. 4. Relation of the density of the reaction product (d_4^{20}), obtained with 61.25% sulfuric acid, (A) to the number of moles of isobutylene absorbed per mole of acid (B). 1) Calculated by the rule of additivity; 2) experimental data.

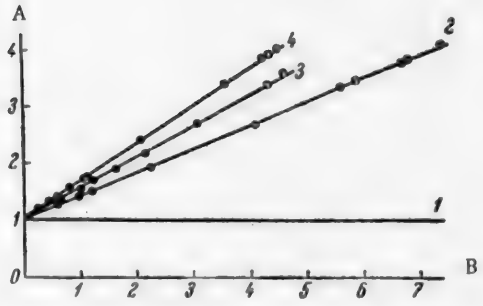

Fig. 5. Relation of the relative volume (in ml) of the reaction products (A) to the number of moles of isobutylene absorbed per mole of acid (B). Volume of reaction products obtained with acid of the following concentrations (in %): 1) original acid; 2) 41.27, 3) 51.39, 4) 61.25.

We can assume that the volumes of the reaction products obeyed the law of additivity. Therefore, it seemed interesting to calculate on the basis of data on the change in density of the reaction products (Table 1, Figs. 2-4) and the increase in their volume with the extent of saturation (Fig. 5) the true density of the product actually formed, present in a mixture with free sulfuric acid when up to one mole of isobutylene was absorbed per mole of acid in solution, and in a mixture with isobutylsulfuric acid and tertiary isobutyl alcohol at a higher degree of saturation.

It was assumed that the original sulfuric acid and the isobutylsulfuric acid obtained were hydrated to the same extent and that the tertiary alcohol formed probably solvated the isobutylsulfuric acid. Thus, it was assumed that for a degree of reaction up to 1:1 (moles), the isobutylene reacted with sulfuric acid to form either isobutylsulfuric acid alone or some of the latter and the tertiary alcohol, which remained in the solvation envelope of the isobutylsulfuric acid or the sulfuric acid. The same assumption was also made for cases with a higher degree of saturation, considering that isobutylene was added to the hydrated isobutylsulfuric acid formed in the previous stage to form the tertiary alcohol, which remained in the solvation envelope of the isobutylsulfuric acid.

TABLE 2

Calculation of the Density of the Reaction Products

	Extent of reaction, C_4H_8 : H_2SO_4 (moles)	
	0.4 : 1	1.4 : 1
Relative volume from Fig. 5 (in ml)	1.17	1.59
Initial volume in given section (in ml):		
at 0 : 1 mole	1.00	–
at 1 : 1 mole	–	1.42
Increase in volume (in ml) v_1	0.17	0.17
Total moles reacted in same section (0.0055 · 0.4)	0.0022	0.0022
Isobutylene reacted × 56 = p_1g	0.1240	0.1240
Hydrated acid reacted × 237.5 = p_2g	0.526	–
Hydrated isobutylsulfuric acid reacted × 293.5 = p_3g	–	0.650
Volume of acid reacting : 1.314 = v_2 ml	0.400	–
Volume of isobutylsulfuric acid reacting : 1.148 = v_3 ml	–	0.567
Characteristics of reaction product formed in solution:		
Volume V (in ml):		
$v_1 + v_2$	0.570	–
$v_1 + v_3$	–	0.737
Weight P (in g):		
$p_1 + p_2$	0.650	–
$p_1 + p_3$	–	0.774
Density:		
calculated (d = P/V)	1.140	1.050
found at 1 : 1 (moles)	1.148	–
found at 2 : 1 (moles)	–	1.058

We think it necessary to present the method of calculating the density of the reaction product formed, present in solution.

The calculation was based on the fact that the reaction products obtained—a mixture of isobutylsulfuric acid and tertiary alcohol and, in the earlier stages, unreacted sulfuric acid also—has a larger volume than the original acid. The increase in volume is wholly due to the reaction product formed, namely, isobutylsulfuric acid, hydrated or partially solvated with the tertiary alcohol. This makes it possible to calculate the volume of the reaction product formed and, knowing the amount of isobutylene that reacted and consequently, the weight of the product obtained, we can calculate its density.

We give an example of the calculation for the reaction products obtained from 41.27% sulfuric acid (1 ml) at the degrees of saturation 0.4 : 1 (moles) and 1.4 : 1 (moles).

1 ml of sulfuric acid of the given concentration (d_4^{20} = 1.314) contains 0.0055 mole of acid.

The average molecular weight of hydrated sulfuric acid, which consists of a mixture of hydrates ($H_2SO_4 \cdot 7.75\ H_2O$) is 237.5.

The average molecular weight of isobutylsulfuric acid hydrated to the same degree ($C_4H_9OSO_2OH \cdot 7.75H_2O$, d_4^{20} 1.148) is 293.5 (Table 2).

The calculation presented shows that in all cases in the interaction of isobutylene first with sulfuric acid and then with the reaction product, obtained in the previous stage, the density of the actual product formed is

TABLE 3

Amount of Water Reacting During the Process

Initial sulfuric acid		C_4H_8 absorbed (in moles per mole of acid)	Water reacting	
concentration (in %)	average composition of hydrate		in moles per mole of acid	in %
41.27	$H_2SO_4 \cdot 7.75\ H_2O$	7.40	6.40	83
51.39	$H_2SO_4 \cdot 5.15\ H_2O$	4.62	3.62	70
61.25	$H_2SO_4 \cdot 3.45\ H_2O$	4.51	3.51	~101

considerably below that of the reaction product as a whole (Figs. 2-4, curves 1). The calculated value of the density remained at one level and equaled the density of the reaction product observed when a mole of sulfuric acid absorbed whole numbers of moles of isobutylene.

This confirms the accuracy of the density calculation.

DISCUSSION OF RESULTS

The stepwise character of the curves (Figs. 2-4, curves 1) constructed from calculated data on the density of the actual reaction product formed indicates that the densities of mixtures of these products obey the law of additivity.

Hence we may draw the conclusion that sulfuric and isobutylsulfuric acids are hydrated to the same degree and that the concentration of sulfuric acid itself and the extent of the process do not change but remain constant. Apparently, the same situation also occurs in other cases of the interaction of unsaturated hydrocarbons (C_2H_4, C_3H_6, n-C_4H_8, etc.) with sulfuric acid to form the corresponding alkylsulfuric acids, so that the free sulfuric acid concentration remains unchanged during the whole time of the reaction.

This agrees with the hypothesis of Dalin, Rashal', and Kasparov [7] that in the sulfuric acid hydration of ethylene the unreacted sulfuric acid remains at the same concentration.

The uniformity of the reaction of isobutylene with sulfuric acid in all of its stages with various amounts of free tertiary alcohol present in the reaction products together with isobutylsulfuric acid, indicates that the isobutylsulfuric acid is probably gradually solvated by molecules of the alcohol formed.

The alcohol formed remains in the solvation envelope of the isobutylsulfuric acid, but the possibility of solvation of free sulfuric acid also cannot be excluded. Recalculation of the data in Table 1 for the maximum extent of the action shows that the greater part of the water present in the system is consumed in the hydration of isobutylene (Table 3).

Attention is attracted by the high degree to which water present in the system is used in the hydration of isobutylene and this reaches 100% when 61.25% acid is used. The higher percent use of water, exceeding the theoretical (~101%), is explained by experimental error and not by the formation of diisobutyl sulfate, which is improbable.

The data obtained show that in this case free water is completely absent and tertiary isobutyl alcohol must be formed by replacement of this in the solvation envelope of isobutylsulfuric acid.

On the basis of the investigation, we propose the following scheme for the reaction of isobutylene with hydrated sulfuric acid, which may be extended to analogous reactions with other gaseous unsaturated hydrocarbons:

$$\text{iso } C_4H_8 + H_2SO_4 \cdot nH_2O \rightleftarrows C_4H_9OSO_2OH \cdot nH_2O,$$

$$\text{iso-}C_4H_8 + C_4H_9OSO_2OH \cdot nH_2O \rightleftarrows C_4H_9OSO_2OH \cdot C_4H_9OH \cdot (n-1)\,H_2O,$$

$$\text{iso-}C_4H_8 + C_4H_9OSO_2OH \cdot C_4H_9OH \cdot (n-1)\,H_2O \rightleftarrows$$

$$\rightleftarrows C_4H_9OSO_2OH \cdot 2C_4H_9OH \cdot (n-2)\,H_2O \text{ etc.}$$

Thus, the formation of both the alkylsulfuric acid and of the corresponding alcohol is explained by the one process of addition of the unsaturated hydrocarbon to the sulfuric acid hydration complex, whereby the formation of the alcohol apparently proceeds through the stage of a carbonium ion [2], though another mechanism is also possible [8, 9].

SUMMARY

1. By an investigation of the electrical conductivity and density of the reaction product obtained by interaction of liquified isobutylene with sulfuric acid at concentrations from 41 to 61%, it was shown that direct hydration of isobutylene occurs and that the process is uniform throughout its whole course.

2. It was found that in the case of 61.25% sulfuric acid, all of the water present in the system may be used entirely in the hydration of isobutylene.

3. The hypothesis is put forward that sulfuric and isobutylsulfuric acids are hydrated to the same degree and that the concentration of free sulfuric acid remains constant during the reaction.

4. The tertiary isobutyl alcohol formed in the given process remains in the solvation envelope of the isobutylsulfuric acid.

5. It was noted that the formation of alkylsulfuric acid and the corresponding free alcohol by reaction of an unsaturated hydrocarbon with sulfuric acid may be explained by a single process of addition of the unsaturated hydrocarbon to the sulfuric acid hydration complex.

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PREPARATION OF TEREPHTHALIC ACID THROUGH p,p'-DIALKYL DERIVATIVES OF DIPHENYLETHANE

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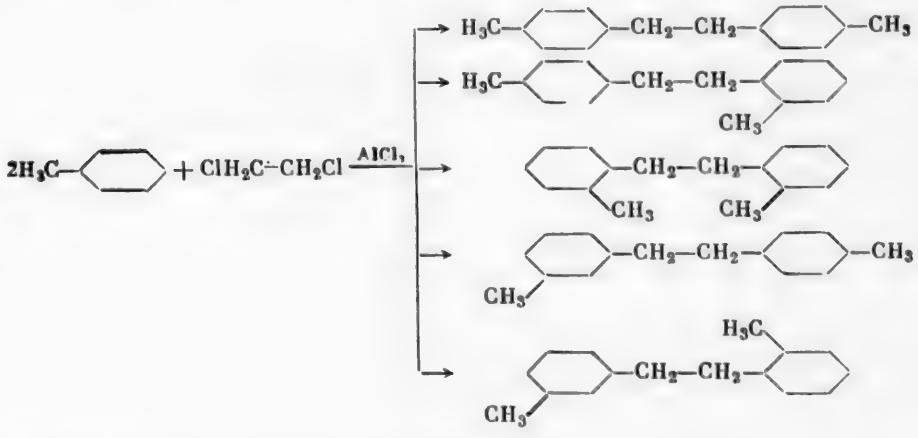
In connection with the development of the production of the synthetic fiber "Lavsan", mentioned in the Seven-Year Plan, the synthesis of terephthalic acid and its dimethyl ester has acquired particular importance.

Most of the methods described in the literature [1-5] for the preparation of terephthalic acid are based on the oxidation of p-xylene with various oxidizing agents. The high cost and low accessibility of this in comparison with some other homologs of benzene sharply decrease the commercial value of these processes. Therefore, we attempted to prepare terephthalic acid from cheaper and readily accessible coal-tar chemical raw material through the synthesis of p,p'-dialkyl derivatives of diphenylethane with their subsequent destructive oxidation to terephthalic acid.

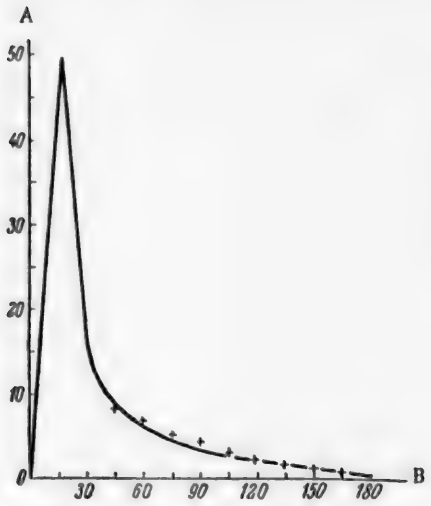
The p,p'-dialkyl derivatives of diphenylethane were synthesized by condensation of symmetrical dichloroethane with monosubstituted homologs of benzene, namely, toluene and cumene, in the presence of aluminum chloride by the Friedel-Crafts reaction.

In the condensation of dichloroethane with toluene one would expect the formation of a considerable amount of the para derivative together with a certain amount of the ortho isomer, while in analogy with other processes of substitution in the aromatic nucleus, one would expect the condensation of dichloroethane with cumene to give almost exclusively p,p'-dialkyl derivatives of diphenylethane.

The condensations of dichloroethane with toluene and cumene proceed according to the equations:



In the condensation it was necessary to consider the possibility of the formation of high-molecular compounds by interaction of the unreacted dichloroethane with the isomeric ditolylethanes formed by the main reactions, which is very undesirable from the point of view of the subsequent preparation of terephthalic acid. Therefore, in all our experiments we used 100% excess of toluene over the calculated amount. The unreacted toluene was used in subsequent experiments.



Determination of the duration of the process (from the rate of evolution of HCl). A) Amount of 1 N NaOH solution (in ml); B) time (in min). V_{titr} - 20 ml = (1/5)V_{abs}.

In choosing temperature conditions for the reaction, we started from the consideration that at an elevated temperature the Friedel-Crafts reaction becomes appreciably reversible and as a result unsubstituted compounds, in particular p,m'-, o,m'-, and even m,m'-ditolylethane, may accumulate in the system. Therefore, the temperature in different experiments varied over the range 40-80°. The duration of the process was determined by the rate of evolution of hydrogen chloride (figure). As a result of the experiments, we raised the yield of isomeric ditolylethanes to 80% and the average yield of dicumylethane was 90% of the dichloroethane taken.

To determine the possibility of using ditolyl- and dicumylethanes for the preparation of terephthalic acid by destructive oxidation, we studied the oxidation with chromic mixture under various conditions. Experiments on the oxidation of ditolyl- and dicumylethanes under optimal conditions made it possible to obtain dicarboxylic acids in 60-65% yield from ditolylethanes and 20% yield from dicumylethane.

The oxidation products of ditolyl- and dicumylethanes were identified by two methods: acidimetric titration and esterification of the dicarboxylic acids obtained with subsequent determination of the melting point. The dimethyl esters of the dicarboxylic acids were prepared by the action of a large excess of methanol in the presence of concentrated sulfuric acid. After two recrystallizations from methanol, the dimethyl ester obtained had a melting point of 140° and a mixed melting point with pure dimethyl terephthalate was not depressed.

When the oxidation product of ditolylethanes was purified by washing with water (at 50°) and alcohol to remove isomeric impurities, on esterification it immediately gave an ester with m.p. 138.5-139.0° and acidimetric titration of it gave 1.99-2.01 equivalents of acid.

Esterification of the unpurified oxidation product of dicumylethane after direct cooling of the reaction mass yielded an ester with m.p. 139.5-140°. A mixed melting point with reagent dimethyl terephthalate was not depressed.

EXPERIMENTAL•

Condensation of dichloroethane with toluene. Into a 400-ml, round-bottomed, two-necked flask, fitted with a bulb condenser and a heeled stirrer and immersed in a water bath, were placed 13.5 g (0.1 mole) of $AlCl_3$, 39.4 (0.5 mole) of dichloroethane, and 212 ml (2 moles) of toluene. The heater and stirrer were switched on simultaneously. During the first hour the temperature was raised to 60°, in the second, from 60 to 75°, and then kept at 75-80° for one hour. The condensation product obtained, a brownish liquid, was poured into 200 ml of water in a beaker and then separated from the slimy water in a separating funnel.

The slimy water was extracted twice with fresh toluene (25 ml portions). The toluene extract was added to the main product. The condensation product was washed once with water, once with hydrochloric acid (1:1), again with water, with 4% soda solution, and again with water and then distilled to remove residual moisture and unreacted toluene. Distillate was collected up to 130°. We obtained 163 ml (137 g) of distillate. After distillation the product was a red-brown liquid which crystallized on standing. The yield was 85 g (0.4 mole) of ditolylethane, representing 90% on the toluene reacting.

The same method was used for the reaction with cumene.

The results of experiments with a dichloroethane to toluene and cumene ratio of 1:4 and a gradual increase in temperature are given in Table 1.

•The following students from the Pharmaceutical Faculty of the Dnepropetrovsk Medical Institute participated in the experimental work: D. S. Glukhova, N. V. Lysenkov, Z. S. Rudneva, O. V. Fomenko, and A. I. Ivanitskii.

TABLE 1

$AlCl_3$ taken (mole/mole of DCE)	Temp. of last hr of condensation (°C)	Duration of reaction (in hrs)	Yield of ditolylethane (in % of theoretical)
0.38	60—65	6.0	71.6
0.20	60—75	6.0	70.0
0.20	70—75	6.0	73.7
0.38	70—75	4.0	73.7
0.20	70—75	4.0	71.2
0.20	70—75	4.0	72.0
0.20	70—75	3.0	79.0
0.20	70—75	3.0	81.0
0.40	85—87	5.0	84.0
0.40	75—80	6.0	92.0
0.40	80—85	6.0	90.0
0.40	80—85	5.0	91.0

The optimal temperature conditions consisted of a gradual rise in temperature to 75° over a period of two hours and maintenance at 75-80° for an hour. Under these conditions the yield of isomeric ditolylethanes reached an average of 80% (on the dichloroethane taken).

The condensation of dichloroethane with cumene over a period of 6 hours and at a maximum temperature of 80-85° gave an average yield of dicumylethane of 90% (on that taken).

Oxidation of Ditolylethanes to Dicarboxylic Acids with Chromic Mixture

Into a 1-liter porcelain beaker fitted with a stirrer and thermometer and immersed in a water bath were loaded 21 g (0.1 mole) of ditolylethane and 160 ml of 50% sulfuric acid, after which the stirrer and heater were switched on. Over a period of 35 minutes 32.8 g (0.14 mole) of finely ground $K_2Cr_2O_7$ was added in small portions. The temperature of the reaction mixture was kept within the range 60-65°. Additions were made in four stages and each time 38 ml of 80% sulfuric acid and 32.8 g of $K_2Cr_2O_7$ were added. The time for each addition at 60-65° was 10 minutes. After the additions the reaction mixture was kept at 70-80° for 40 minutes, at 80-90° for 40 minutes and finally it was boiled gently for 1.5 hours.

The reaction mixture was poured into 400 ml of cold water, heated to 90-95° with stirring, cooled and filtered on a Buchner funnel. The gray-green precipitate was washed with hot water to remove chromium salts and dissolved in a hot solution of sodium carbonate so that there was a clear reaction to Brilliant Yellow paper. The suspension obtained was filtered and the filtrate heated to 70-80° and acidified to Congo with hydrochloric acid (1 : 1). The dicarboxylic acids obtained were collected by filtration and purified. For this purpose, 20 g of dicarboxylic acid paste and 100 ml of water were placed in a 250-ml beaker. The suspension was heated to 50-55° with stirring, kept at this temperature for 50 minutes, and filtered. The precipitate was again washed and then stirred with 50 ml of methanol and separated on a Buchner funnel.

The results of the oxidation experiments are given in Table 2.

The highest yield of acids was achieved with a 30% excess of bichromate and sulfuric acid (over theoretical).

Preparation of dimethyl terephthalate. Into a round-bottomed flask fitted with a stirrer and reflux condenser and immersed in a water bath were placed 4 g of the dicarboxylic acid obtained by the method described above, 47.5 g of methanol, and 11.1 g of H_2SO_4 (d = 1.84).

The reaction mixture was boiled and stirred for 5 hours. The crystals of ester which separated when the mixture was cooled were collected and dried in a vacuum desiccator over concentrated H_2SO_4. We obtained 4.4 g of dimethyl ester with m.p. 138.5-139.0°. The product was white and scaly and did not depress the melting point of reagent dimethyl terephthalate.

TABLE 2

$K_2Cr_2O_7$		H_2SO_4		Oxidation time (in hrs)	Dicarboxylic acids obtained, calculated as phthalic acids (in % theoretical)
taken (in moles)	excess over theoretical (in %)	taken (in moles)	excess over theoretical (in %)		
0.55	50	4.5	100	4	66.0
0.55	50	3.3	50	4	63.0
0.48	30	3.2	67	4	64.7
0.48	30	2.9	50	4	65.0
0.48	30	2.5	30	6	65.0
0.48	30	2.5	30	5	62.0
0.48	30	2.5	30	5	64.9
0.42	15	1.8	15	5	49.0
0.42	15	1.8	15	5	47.2
0.40	10	1.8	10	5	45.1

For acidimetric titration a sample of 0.1643 g of dicarboxylic acids was placed in a 150-ml conical flask and dissolved in 40 ml of 0.1 N NaOH with heating on a water bath. The excess alkali was titrated to phenolphthalein with 0.1 N H_2SO_4. The back titration required 21 ml of 0.1 N H_2SO_4. The equivalent acidity was 2.02 instead of 2.00 (according to theoretical calculation).

SUMMARY

1. In a study of the condensation of dichloroethane with toluene and cumene in the presence of aluminum chloride we obtained a mixture of isomeric ditolylethanes in up to 80% yield on dichloroethane and dicumylethanes in up to 90% yield.

2. The conditions of destructive oxidation of ditolyl- and dicumylethanes with chromic mixture were studied.

3. The yield of dicarboxylic acids from the destructive oxidation of the mixture of isomeric ditolylethanes, calculated as phthalic acids, was 60-65%.

4. In the oxidation of dicumylethane the yield of dicarboxylic acids, calculated as phthalic acids, was 20%.

5. It was established that it was possible to isolate about 70% of terephthalic acid from the oxidation products of the ditolylethanes and about 95% from the oxidation products of dicumylethane.

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PREPARATION OF DIBASIC ACIDS FROM SATURATED MONOBASIC FATTY ACIDS BY OXIDATION WITH NITRIC ACID•

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Nowadays dibasic acids find wide application in the national economy in the production of artificial fibers, alkyd resins, plasticizers, and ester lubricants and for other purposes. In the search for cheap raw materials for the production of dibasic acids, the possibility of using oxidation products of paraffins was studied. In the present work we present the results of investigating the possibility of preparing aliphatic dibasic acids by oxidation of saturated monobasic acids.

Most experimental work on the oxidation of aliphatic monocarboxylic acids was carried out in the last century and was connected with the study of natural products, namely, fats and waxes. All the authors used nitric acid as the oxidant. They showed that the oxidation of monocarboxylic acids yielded dicarboxylic acids. Thus, oxidation of stearic acid yielded suberic, adipic, glutaric, and succinic acids [1]; a mixture of stearic and palmitic acids gave succinic and glutaric acids [2]; myristic acid gave all the acids mentioned above and pimelic acid [3].

Then for a long time interest in the oxidation of fatty acids waned and only increased again very recently in connection with the great need for dicarboxylic acids already mentioned. Thus, Euler, Hasselquist and Löov [4] studied the oxidation of stearic acid with a mixture of nitric and sulfuric acids. Among the dibasic acids obtained, they were able to identify brassylic, sebacic, azelaic, suberic, and adipic acids. The yield of these acids was low and the balance was not given. Kobayashi [5] heated capric acid with 30% nitric acid in a sealed tube at 170-175°. He isolated succinic, glutaric, and pimelic acids. Petrov and Grigor'ev [6] oxidized the acids obtained by oxidation of paraffin with atmospheric oxygen. The acids contained a large amount of unoxidized paraffin. The oxidation was carried out with nitric acid of sp.g. 1.36 with heating. The authors obtained only 7.4% of dicarboxylic acids with an acid number of 880 and an average molecular weight of 128.

There are only a few patents on the preparation of dicarboxylic acids by oxidation of monocarboxylic acids. Thus, according to Raccke and Busse [7], dicarboxylic acids are obtained from monocarboxylic acids by oxidation of the latter at no higher than 120° with nitric acid in the presence of not less than 10% of sulfuric or phosphoric acids. In another patent, the same authors [8] recommend the oxidation of monocarboxylic acids with 86% nitric acid in the presence of ammonium vanadate.

According to Köegler [9], dicarboxylic acids are obtained from monocarboxylic acids by oxidation of the latter with 90% nitric acid. Engleri, Alto, and Richards [10] oxidized monocarboxylic acids with 10-30% nitric acid at 100-250° and a pressure of 3.5-35 atm. An example was given in the patent and according to this the oxidation of palmitic acid gave a mixture of C_4–C_{14} dibasic acids.

We studied the oxidation of the C_7–C_9 fraction of saturated monobasic fatty acids obtained by oxidation of paraffins. The nitric acid oxidation was carried out by two methods: boiling with nitric acid and treatment

•Communication 1 of a series of papers on the preparation of dibasic acids from oxidation products of paraffins.

with superheated nitric acid vapor. Both these methods of oxidation gave a good yield of dicarboxylic acids. When boiled with nitric acid, a considerable part of the monobasic acids did not undergo oxidation and could be returned to a second oxidation.

In view of the very low gas formation, reoxidation should lead to very high yields of dicarboxylic acids. In the oxidation with superheated nitric acid vapor, due to the high temperature the monobasic acids were oxidized more completely under the experimental conditions, and side reactions were of great importance. The dibasic acids obtained consisted of a mixture of succinic, glutaric, adipic, and pimelic acids. Oxalic acid was present in very small amounts.

EXPERIMENTAL

Starting raw material. We studied the oxidation of a C_7–C_9 fraction of monobasic acids isolated from uniform commercial fraction of fatty acids from the Shebekino plant. Distillation of the commercial fraction showed that it contained a considerable amount of head and tail fractions. It was therefore vacuum distilled and 60% of the required C_7–C_9 fraction with an acid number of 380 and an ester number of 33 was collected at 139-148° and 40-45 mm Hg.

Analysis method. The composition of the mixtures of dibasic acids obtained was determined by partition chromatography on silica gel. The method was basically that of Marvel and Rands [11] with some modifications proposed by Higuchi [12] and Bove and Raveux [13] MSK grade silica gel from the Voskresensk plant was used for the analysis.

The dicarboxylic acids were eluted with chloroform containing successively increasing concentrations of n-butyl alcohol (3, 5, 10, and 20%).

The concentration of spent nitric acid in the aqueous layer in the presence of monobasic and dibasic acids was determined by titration in the presence of Tropeolin 00. The organic acids were not titrated under these conditions. It was established that when solutions of nitric acid were titrated to a yellow color with Tropeolin, 0.015 N nitric acid remained untitrated in the solution. The content of lower monobasic acids in the distilled nitric acid was determined by stepwise titration of the aqueous distillates first to an orange color with Methyl Orange and then with Thymol Blue. It was possible to use Methyl Orange for titration under these conditions as the stronger dibasic acids were absent from the solution.

Oxidation of Monobasic Fatty Acids by Boiling with Nitric Acid

The C_7–C_9 fraction was oxidized with 50% nitric acid.

Into a round-bottomed pyrex flask with a reflux condenser with a ground-glass joint were placed 50 g of C_7–C_9 acids and 450 g of 50% nitric acid and boiled for a given time. After the boiling period, the aqueous layer, which contained dibasic acids, lower monobasic acids and spent nitric acid, was separated from the upper, oily layer, which was a mixture of unreacted starting acids and water-insoluble reaction products. The bulk of the nitric acid and the lower acids were removed from the aqueous layer by distilling it to 1/3 of the original volume. The residue was poured into a porcelain dish and evaporated on a water bath until all the water had been removed. Then a fresh portion of water was added and the mixture again evaporated until all the water had

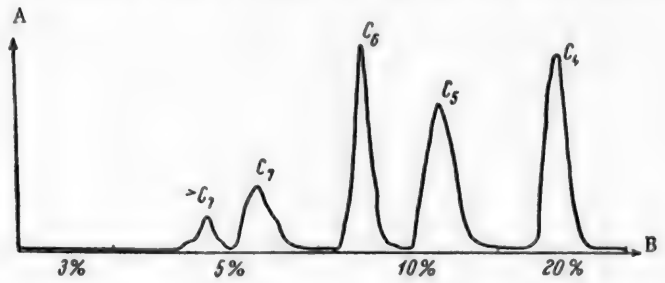

Fig. 1. Chromatogram of "crude" dibasic acids after 30-hours oxidation. A) Amount of 0.01 N NaOH solution (ml); B) amount of eluent (ml).

TABLE 1

Experiments on the Oxidation of the C_7-C_9 Fraction of Monobasic Fatty Acids by Boiling with HNO_3

Oxidation time (in hours)	Yield (in weight % on starting material)		
	dicarboxylic acids		upper layer
	"crude"	chromatographed	
10	38.0	27	60.0
30	45.0	32	52.0

been removed. This operation was repeated several times until the smell of nitric acid and lower acids became almost imperceptible. On cooling, the contents of the dish solidified to a white crystalline mass—the so-called "crude" dibasic acids.

Table 1 gives the yields of dibasic acids obtained by oxidation of the C_7-C_9 fraction of fatty acids for 10 and 30 hours. Table 2 gives the characteristics of the reaction products. Figure 1 shows a chromatogram of the "crude" dibasic acids obtained by oxidation for 30 hours.

Abotu 70% of dicarboxylic acids were found in the "crude" dibasic acids by chromatographic analysis. The residue consisted of some other compounds. This was also indicated by the ester numbers of the "crude" dibasic acids. The compositions of the dibasic acids obtained by 10- and 30-hours oxidation were found to be similar.

The dibasic acids obtained were a mixture of succinic, glutaric, adipic, pimelic and a small amount of acids with a chain of more than seven carbon atoms. Oxalic acid was formed in small amounts (1-1.5%).• Malonic acid was not detected. The nitric acid concentration after oxidation fell to 38-40%.

Oxidation of Monobasic Fatty Acids with Superheated Nitric Acid Vapor

The same C_7-C_9 fraction of monobasic acids was oxidized. The oxidation was carried out with commercial 57% nitric acid in various weight ratios to the raw material taken (1.5 and 2.5)•• and at various temperatures (150-160, 180-190 and 190-200°). Since the oxidation proceeded with the evolution of heat the rate of addition of drops of nitric acid was limited to that required to maintain the given experimental temperature. The duration of an experiment at a ratio of 1.5 was 6-7 hours and at a ratio of 2.5, up to 10-12 hours The apparatus used for the oxidation is illustrated in Fig. 2.

TABLE 2

Characteristics of Oxidation Products

Duration of oxidation (in hrs)	"Crude" dibasic acids								Upper layer	
	acid number	ester No.	% chromatographed	composition of chromatographed acids (in %)					acid number	ester No.
				C_4	C_5	C_6	C_7	$>C_7$		
10	657	15	70	23	25	33	13	6	402	65
30	649	17	70	26	28	26	14	6	410	20

•Determined by titration with potassium permanganate.

••Calculated on 100% nitric acid.

TABLE 3

Oxidation of C_7–C_9 Monobasic Fatty Acids with Nitric Acid Vapor

Expt. conditions			Reaction products								
			*Crude dicarboxylic acids			upper layer			aqueous condensate		
									HNO_3		lower fatty acids** (wt. % on original material
Expt. No.	temp. (in °C)	HNO_3* C_7-C_9 fraction (wt.)	wt. % on original starting material	acid number	ester number	wt. % on original starting material	acid number	ester number	in % of that taken	concentration (%)	
1	190—200	1.5	26.6	590	130	26.6	296	224	15.7	11.0	14.0
2	180—190	1.5	41.0	620	106	42.5	290	253	18.0	14.3	12.6
3	150—160	1.5	34.2	594	132	56.6	292	236	18.2	19.5	3.0
4	180—190	2.5	56.3	680	85	4.0	250	270	18.2	14.6	18.8
5	150—160	2.5	46.3	614	121	27.3	274	270	25.0	20.4	13.6

* Calculated on 100% nitric acid.

** Calculated on acetic acid.

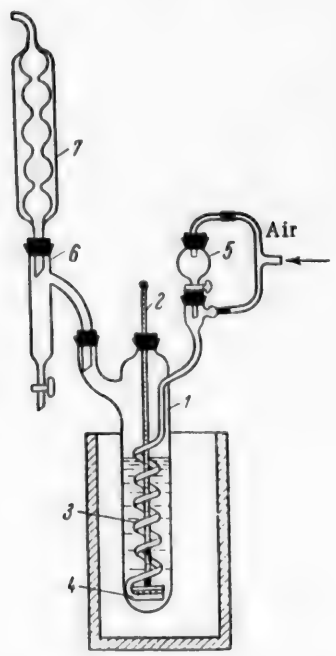

Fig. 2. Plan of oxidation apparatus. 1) Reactor; 2) thermometer; 3) spiral; 4) porous disc; 5) dropping funnel; 6) trap; 7) reflux condenser.

The experimental procedure was as follows. The starting material (100 g) was placed in the cylindrical glass reactor 1 with a thermometer 2 and heated by the spiral 3, fitted with a Schott porous disc 4. Nitric acid was added dropwise under an air pressure from dropping funnel 5, connected to the upper end of the spiral. The reaction gases and water vapor with entrained monobasic acids passed through the outlet tube into trap 6, fitted with a reflux condenser 7. The aqueous condensate was run off periodically and the acids returned to the oxidation in the reactor. The reactor was heated on an air bath with an electric heater.

The oxidation products were a homogeneous liquid from which the "crude" dibasic acids were extracted with hot water. The reaction products which were insoluble in hot water (upper layer) contained hardly any of the original monobasic acids.

Thus, treatment of the latter with ligroin showed that the percent of monobasic acids which were soluble in ligroin was low and not more than 2-3%. The upper layer from the experiment was reoxidized by boiling with 57% nitric acid in a flask with a reflux condenser. The weight ratio of nitric acid to the upper layer was 4.5.

Boiling for 6 hours and evaporation of the aqueous layer yielded a further amount of "crude" dibasic acids. The aqueous condensate contained spent nitric acid and water-soluble monobasic acids, formed as a result of the oxidation.

TABLE 4

Reoxidation of Upper Layers

Oxidation products					
"crude" dicarboxylic acids			upper layer		
in weight % on original C_7–C_9 fraction	acid number	ester number	in weight % on original C_7–C_9 fraction	acid number	ester number
13.0	616	34	2.7	360	125
24.0	625	100	5.8	336	199
15.1	538	147	13.6	400	128
14.8	415	222	7.7	290	248

Table 3 gives data on the oxidation of the C_7–C_9 fraction. Table 4 gives the results of reoxidation of the upper layers from corresponding experiments. According to chromatographic data, 70% of the "crude" dibasic acids obtained consisted of dibasic acids. The latter were a mixture of succinic (~32%), glutaric (~30%) adipic (~22%), pimelic (~12%), and acids higher than C_7 (~4%). The dibasic acids obtained under the most drastic oxidation conditions at 180-190° and a ratio of 2.5 were exceptional. In this case the succinic acid content of the mixture increased strongly (up to 50%).

DISCUSSION OF RESULTS

As the result obtained show, the oxidation of the fraction of C_7–C_9 fatty acids with nitric acid yielded pimelic, adipic, glutaric, and succinic acids and a small amount of acids above C_7 and oxalic acid; malonic acid was not found. The yield of dibasic acids that could be chromatographed in oxidation with nitric acid by boiling for 30 hours was 32% or more than 65% by weight on the acids reacting. In experiments on oxidation by nitric acid vapor, for example experiment No. 2 (Tables 3 and 4), the yield of "crude" dicarboxylic acids was 65% (together with acids obtained by reoxidation of the upper layer) or 45%, calculated on the "crude" dibasic acids, 70% of which were chromatographed. Both methods of oxidizing fatty acids have their merits and drawbacks. Treatment of fatty acids with boiling nitric acid is characterized by little formation of gaseous and steam-volatile products, as a result of which, reoxidation of the residual unreacted upper layer may be expected to give high yields of the desired product.

A drawback of the method is the duration of the actual oxidation process and mainly, the need for distilling large amounts of nitric acid to isolate the dibasic acids.

The second method does not have the latter drawback as the unreacted nitric acid distills during the oxidation process. The final oxidation products are obtained free from nitric acid.

The drawback of this method is the increased formation of side products, both gaseous and steam volatile (volatile fatty acids). The latter distilled during the oxidation process together with unreacted nitric acid. Separation of this mixture for further use of the components was difficult. As regards the composition of the dicarboxylic acids obtained, in experiments with boiling with nitric acid the proportions of the separate dicarboxylic acids changed little with the degree of oxidation. In experiments on oxidation with superheated nitric acid vapor, we were unable to establish a clear relation between the conditions and the change in composition of the dicarboxylic acids obtained. We only noted some increase in the succinic acid content of the oxidation products with an increase in the oxidation temperature and the amount of nitric acid taken. It seems more profitable to us to study these problems on individual monobasic fatty acids.

SUMMARY

In a study of the oxidation of a fraction of C_7–C_9 monobasic fatty acids by two methods, namely, boiling with nitric acid and treatment with superheated nitric acid vapor, it was found that in oxidation by both methods the main reaction product was a mixture of pimelic, adipic, glutaric, and succinic acids.

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PREPARATION OF ISONICOTINIC ACID FROM THE LOW-BOILING FRACTION OF COAL-TAR BASE

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Isonicotinic (4-pyridinecarboxylic acid is the starting material for the preparation of isonicotinohydrazides (phthivazid, etc.), which are widely used as pharmaceutical preparations for treating tuberculosis.

Light pyridine bases extracted from coke-oven gas are the main source of raw material for preparing isonicotinic acid. Rectification of the former gives a so-called β-picoline fraction, whose main components are β-picoline, γ-picoline, and 2, 6-lutidine. The picolines in this mixtures are separated from 2, 6-lutidine in the form of water-soluble complex salts with zinc chloride. Decomposition of the complex salts isolated gives a mixture of β- and γ-picolines, oxidation of which gives a mixture of isomeric nicotinic acids. To prepare isonicotinic acid, Graf [1] used the capacity of γ-picoline to form with formaldehyde mono-, di-, and tri-(hydroxymethyl) derivatives, which are readily oxidized by nitric acid to isonicotinic acid. As β-picoline does not react with formaldehyde it is readily separated from the hydroxymethyl derivatives of γ-picoline. Rubtsov and his co-workers [2] refined the method for preparing isonicotinic acid from the β-picoline fraction.

The importance of isonicotinohydrazides and the limited sources of γ-picoline for their production create a need for finding new forms and sources of raw material for the preparation of isonicotinic acid. Swietoslawcki and Bylicki [3] proposed the use of 2, 4-lutidine and 2, 4, 6-collidine, which, on oxidation and removal of the carboxyl groups in positions 2 and 6, give isonicotinic acid. Rubtsov and his co-workers [4, 5] studied the possibility of preparing isonicotinic acid from the trimethyl ester of citric acid through the intermediates 2, 6-dihydroxynicotinic and 2, 6-dichloroisonicotinic acids. Reduction of 2, 6-dichloroisonicotinic acid in the presence of a skeletal catalyst at 15 atm gave isonicotinic acid in a yield of 78% of theoretical (on 2, 6-dichloroisonicotinic acid).

One of the sources of raw material for the preparation of isonicotinic acid may be the low-boiling fraction of coal-tar bases, which contains a series of alkylpyridines. Some of these alkylpyridines may be oxidized and decarboxylated to give isonicotinic acid. Table 1 lists the alkylpyridines contained in coal-tar bases and the possible products of oxidation and decarboxylation of the former. As is known, the carboxyl groups in positions 3, 4, and 5 in pyridinecarboxylic acids are stable, while those in positions 2 and 6 are readily removed. Decarboxylation proceeds quite rapidly during the oxidation of alkylpyridines with sulfuric acid. Thus, 7 of the 28 alkylpyridines given in Table 1 may be converted to isonicotinic acid by oxidation and decarboxylation.

The similar physical and chemical properties of alkylpyridines and the lack of methods for determining them quantitatively in coal-tar bases hinders the separation and use of those alkylpyridines which could give isonicotinic acid. In this connection it seemed interesting to oxidize narrow fractions of alkylpyridines and to isolate isonicotinic acid from the oxidation products. The author carried out investigations in this direction and the results are given in this article.•

EXPERIMENTAL

The starting materials for the investigation were heavy pyridine bases, isolated under industrial conditions from the naphthalene (light-medium) fraction of coal tar. The crude bases were dissolved in 25% sulfuric acid to

•T. M. Markacheva participated in the experimental work.

TABLE 1

Alkylpyridines Identified in Coal-Tar Bases [6]

Alkylpyridine	Boiling point (in °C)	Oxidation and decarboxylation products
α-Picoline	129.4	Pyridine
β-Picoline	144	Nicotinic acid
γ-Picoline	145.3	Isonicotinic acid
2,6-Lutidine	144	Pyridine
2,3-Lutidine	160.3	Nicotinic acid
2,4-Lutidine	158	Isonicotinic acid
2,5-Lutidine	157	Nicotinic acid
3,5-Lutidine	169.5	Dinicotinic acid
3,4-Lutidine	162-163	Cinchomeronic acid
α-Ethylpyridine	148.7	Pyridine
β-Ethylpyridine	165.5-166	Nicotinic acid
γ-Ethylpyridine	165	Isonicotinic acid
2-Methyl-6-ethylpyridine	150-151	Pyridine
2-Methyl-4-ethylpyridine	178.8	Isonicotinic acid
2-Methyl-3-ethylpyridine	195-6(753)	Nicotinic acid
2-Methyl-5-ethylpyridine	174.6	Nicotinic acid
2-Ethyl-4-methylpyridine	178.7	Isonicotinic acid
2,3-Dimethyl-6-isopropylpyridine	197.4-197.8 (747)	Nicotinic acid
2,3,4-Collidine	168	Cinchomeronic acid
2,4,5-Collidine	167	Cinchomeronic acid
2,4,6-Collidine	170.3	Isonicotinic acid
2,3,6-Collidine	172.8	Nicotinic acid
2,3,5-Collidine	186.8	Dinicotinic acid
2,4-Dimethyl-6-ethylpyridine	164.2-1.66.4 (575)	Isonicotinic acid
2,6-Dimethyl-4-ethylpyridine	184-186	Pyridine
2,3,4,6-Tetramethylpyridine	203 (750)	Cinchomeronic acid
2 3,4,5-Tetramethylpyridine	233	3,4,5-Pyridinetricarboxylic acid
2,3,5,6-Tetramethylpyridine	130-132 (100)	Dinicotinic acid

remove neutral oils and tarry substances. The base sulfate obtained was washed twice with xylene in which the traces of oils and tarry substances dissolved. After purification with xylene, the base sulfate was decomposed with 20% sodium hydroxide solution to give pure bases.

The starting crude bases had the following characteristics: d_4^{20} 1.057, base content 79.8% (calculated on 88.9% anhydrous product), water content 10.2%, neutral oils and tarry substances 10.0%; boiling range (in °C): 10% 199.8, 20% 211.4, 30% 219.8, 40% 226.2, 50% 230.4, 60% 233.6, 70% 235.8, 80% 237.8, 90% 242.1, 96% 252.7. After removal of the neutral oils and tarry substances and drying with solid sodium hydroxide the bases had the following characteristics: d^{20}_4 1.063, base content 99.8%; boiling range (in °C): 10% 208.0, 20% 217.6, 30% 223.6, 40% 228.8, 50% 232.1, 60% 234.2, 70% 236.3, 80% 238.4, 90% 241.6, 96% 284.3.

The low-boiling fractions for preparing isonicotinic acid were separated by fractionating the purified bases on a laboratory fractionation apparatus with an efficiency of 36 theoretical plates (on a benzene-dichloroethane mixture). We described the design of this column in [7]. The fractions were taken off in small portions, each representing about 1.5-2% by weight of the charge. The specific gravities, molecular weights, and boiling ranges of the fractions were determined. The yields and characteristics of the fractions obtained are given in Table 2.

TABLE 2

Fractionation of Purified Bases of the Naphthalene Fraction

Fraction No.	Take-off temp. (in °C)	Fraction yield (in wt. %)	Fraction characteristics							
			d_4^{20}	molecular wt.	boiling point (°C) during distillation (%)					
					start	10	30	50	80	90
					Hydrates					
1	96.6	0.59	0.9095	—				—	—	—
2	—	1.47	—	—	126.6	131.8	136.0	138.4	144.5	151.6
3	142.3	1.61	0.9450	102	139.3	143.5	145.5	147.6	150.2	152.8
4	153.6	1.63	0.9399	104	142.4	150.7	152.3	153.4	155.9	157.0
5	160.3	1.72	0.9363	109	148.8	157.8	159.4	160.4	162.4	164.9
6	166.5	1.85	0.9339	112	162.5	164.0	164.7	165.5	167.5	170.2
7	173.7	1.87	0.9415	114	168.5	170.7	171.7	172.2	175.7	177.8
8	182.5	2.05	0.9798	107	179.3	179.4	180.7	181.2	183.0	184.0
9	183.6	1.70	0.9920	106	182.5	183.5	184.0	184.6	185.4	186.1
10	186.7	1.77	0.9918	102	184.0	185.1	185.6	186.1	187.1	188.7
11	192.8	1.99	0.9894	109	188.4	189.7	190.4	190.9	193.0	196.0
12	200.0	2.11	0.9870	112	195.3	196.1	197.1	197.6	199.6	201.0
13	203.1	2.08	0.9893	115	199.1	200.1	200.3	201.1	202.1	202.6
14	205.2	2.04	0.9956	116	201.8	202.2	202.8	202.8	203.8	204.8

The fractions obtained were oxidized to pyridinecarboxylic acids with concentrated sulfuric acid in the presence of selenium [8]. Oxidation by this method proceeds under drastic conditions, and as a result the carboxyl groups formed in positions 2 and 6 are removed during the reaction. The fractions were oxidized in the following way. To a 10 g sample of bases were added 100 g of concentrated sulfuric acid and 0.5 g of selenium powder. The reaction mixture was heated in a 250-ml flask until 90% of the total theoretical amount of water had distilled and at this, the temperature of the reaction mixture reached 280-325°. The water vapor evolved during the reaction was condensed and collected in a trap, and the sulfur dioxide was trapped in an alkaline solution. Except for cinchomeronic acid, the pyridinecarboxylic acids obtained in the reaction were isolated from the reaction mixture in the form of copper nicotinate, isonicotinate and dinicotinate. The copper salt of cinchomeronic acid, which is readily water-soluble, was removed with the filtrate. The free pyridinecarboxylic acids were prepared from their copper salts by decomposition of the latter with 40% sodium hydroxide and neutralization of the excess alkali and acidification of the solution with concentrated hydrochloric acid. After removal of the carboxyl groups in positions 2 and 6 and separation of the cinchomeronic acid, only a mixture of isomeric nicotinic and dinicotinic acids could be precipitated from the hydrochloric acid medium. The experimental results on the oxidation of low-boiling base fractions are given in Table 3.

The dinicotinic acid content of the mixture of pyridinecarboxylic acids was determined by dissolving a sample of the latter in water and titrating the solution obtained with 0.1 N sodium hydroxide solution (to phenolphthalein). The mononicotinic and dinicotinic acid contents were determined from the alkali consumption. The data given in Table 3 show that the pyridinecarboxylic acids obtained contained practically no dinicotinic acid, and the products isolated were mixtures of isomeric nicotinic acids. This made it possible to use the melting point diagram of the system nicotinic acid–isonicotinic acid [9] for determining the contents of each of these isomers in the total mixture, as there are no analytical methods for determining nicotinic acids. As the system nicotinic acid–isonicotinic acid forms a eutectic, in addition to determining the melting point of the mixture of acids, we determined the melting point of this mixture with the addition of pure nicotinic and isonicotinic acids to find the corresponding branch on the diagram.

With the exception of fraction No. 1, which was a mixture of base hydrates that distilled below 100°, all the fractions from the fractionation were oxidized. Isonicotinic acid, with traces of nicotinic acid, was isolated from fractions 2, 3, 4, 5, and 6, which boiled at up to 170°. Neither isomeric nicotinic or dinicotinic acids were isolated from the oxidation products of the remaining, higher-boiling fractions. Apparently, oxidation of these fractions and decarboxylation of their oxidation products gave mainly cinchomeronic acid and pyridine.

TABLE 3

Oxidation of Low-Boiling Fractions of Coal-Tar Bases

Expt. No.	Fraction	Boiling range (in °C)	Oxidation sample (in g)	Crude isonicotinic acid obtained		Melting point (in °C)	Content (%)		
				mg	%		monoacid, calc. from NaOH consumed in titration	isonicotinic acid	nicotinic acid
1	No.2	127—152	10.0	0.6	6.0	304.5	100.3	84.6	14.7
2	No.3	139—153	10.0	2.4	24.0	308	100.7	87.4	10.1
3	No.4	142—157	10.0	2.8	28.0	305.5	100.2	85.6	13.9
	Mixture:								
4	Nos. 5 и 6	149—170	10.0	1.78	17.8	309—310	99.6	91.0	9.0
5	Nos. 7, 8, 9, 10	168—189	10.0	Not obtained					
6	Nos. 11, 12, 13, 14	188—205	10.0	Not obtained*					
7	Nos. 2, 3, 4, 5, 6	127—170	10.0	2.2	22.0	306	99.9	86.8	13.2
8	Fraction of crude bases	120—160	10.0	2.2	22.0	305	99.7	85.0	15.0
9		160—200	10.0	Traces					

The pyridinecarboxylic acids isolated from the oxidation products of fractions No. 2, 3, 4, 5, and 6 contained from 85 to 91% of isonicotinic acid and from 9 to 15% of nicotinic acid. Such products satisfy existing technical requirements for isonicotinic acid and could be used for the synthesis of hydrazides.

We also oxidized fractions boiling over a wide temperature range, which were obtained during the fractionation of both purified and crude bases of the coal-tar naphthalene fraction. In experiment 7, a mixture of fractions 2, 3, 4, 5, and 6, boiling over the range 127-170°, was oxidized. The mixture of pyridinecarboxylic acids isolated from the oxidation products contained 86.8% of isonicotinic and 13.2% of nicotinic acids. The yield of this product, relative to the fraction taken for oxidation, was 22%. An equal yield of a product containing 85% of isonicotinic and 15.0% of nicotinic acids was obtained from a fraction of the crude bases boiling over the range 120-160°. This indicated that for the preparation of isonicotinic acid from the low-boiling part of coal-tar bases, the latter need not be freed from neutral oils and tarry substances, which are oxidized vigorously by concentrated sulfuric acid in the presence of selenium. Oxidation of the fraction of crude bases boiling over the range 160-200° gave traces of isonicotinic acid.

The experimental data obtained indicate the possibility of using the low-boiling part of coal-tar bases as the raw material for preparing isonicotinic acid. The yield of technical product was quite high—22% on the crude material oxidized. In comparison, the yield of isonicotinic acid from the β-picoline fraction was 1.5-2.0% of the light pyridine bases. This yield may be increased to 3.0% by isolating and using a fraction containing 2,4-lutidine and 2,4,6-collidine. Thus, the low-boiling part of coal-tar bases is a more concentrated raw material for the preparation of isonicotinic acid than light pyridine bases. A comparison of these forms of raw material shows that by use of the low-boiling part of coal-tar bases, the raw material source for the preparation of isonicotinic acid could be increased by 60-70%.

SUMMARY

1. Isonicotinic acid with melting point 305-310°, containing 85-91% of the main material and 9-15% of nicotinic acid, was isolated from the oxidation products of the low-boiling part of coal-tar bases boiling at up to 170° through its copper salt. The yield of technical isonicotinic acid was 22% on the fraction oxidized.

2. Neutral oils and tarry substances did not interfere with the oxidation of the low-boiling part of the bases, so that the crude bases did not require purification.

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SYNTHESIS OF ISOPRENE AND PIPERYLENE BASED ON n-BUTYLENES AND FORMALDEHYDE•

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For a number of years work has been done in our laboratory on the synthesis of isoprene, based on isobutylene and formaldehyde, and of butadiene, based on propylene and formaldehyde [1]. The starting materials for the preparation of these dienes were alkyl-1,3-dioxanes, which were the main products of the reaction of olefins with formaldehyde in an aqueous medium in the presence of acid [2]. When the alkyldioxanes were passed over catalysts in a mixture with water vapor, they underwent smooth cleavage to give good yields of dienes.

We previously showed that n-butylenes react smoothly with formaldehyde (as formalin) in the presence of sulfuric acid [2]. The main reaction product, obtained in 90% yield, was a mixture of isomeric dioxanes—4, 5-dimethyl-1, 3-dioxane (I) from 2-butene and 4-ethyl-1, 3-dioxane (II) from 1-butene. It seemed interesting to study in greater detail the catalytic conversion of these alkyldioxanes to dienes.

Conditions for Catalytic Conversion of a Mixture of Isomeric Alkyldioxanes (I) and (II)

The mixture of alkyldioxanes diluted with steam was catalytically cleaved over "KSD" catalyst, which consists of a mixture of calcium phosphates. This catalyst was found to be the best of those tested for conversions of alkyl-1,3-dioxanes to dienes [1]. As in the preparation of other dienes, this catalyst required regeneration with a steam-air mixture after each 2-4-hour operating period to restore the activity (by burning off carbonaceous deposits). Satisfactory diene yields were obtained only when the alkyldioxanes were considerably diluted with steam, which we ascribe to the reaction mechanism.

Figure 1 gives the experimental results of investigating the effect of an "arbitrary" contact time (which also means space velocity) on the reaction product yields at 375° and constant steam dilution (dioxane to steam ratio of 1: 3 by weight).

Figure 2 illustrates the effect of varying the temperature over the range 350-450° and varying the contact time (with constant dilution) on the conversion of dioxanes to unsaturated hydrocarbons.

The data given indicate that the total yield of unsaturated hydrocarbons and dienes increases rapidly with an increase in contact time, reaching a maximum at a definite contact time (and consequently, space velocity) for each temperature. The diene content of the total unsaturated hydrocarbons remained constant and did not depend on contact time. The reactions resulting in the formation of dienes and n-butylenes are apparently parallel, but differ greatly in rate. The curve of the unsaturated alcohol yield passes through a maximum that is characteristic of a consecutive reaction as unsaturated alcohols are apparently subsequently dehydrated to dienes. The curve showing deposition of "carbon" on the catalyst gradually rises with an increase in contact time.

•Communication III in a series of papers on diene synthesis based on olefins and aldehydes.

TABLE 1

Catalytic Cleavage of a Mixture of Alkyldioxanes (I) and (II) on a "KSD" Catalyst at 375° and Different Degrees of Steam Dilution

Input space velocity (in ml/ml cat. hr)		Alkyldioxanes: H_2O ratio		Arbitrary contact time (in sec)	Conversion of alkyldioxanes (I) and (II) to unsaturated hydrocarbons (dienes + olefins)	Yield (mol. %) on mixture of alkyldioxanes (I) and (II) passed				Diene content of unsaturated hydrocarbons of contact gas (in vol. %)	Formaldehyde recovered (in % of theoretical)
alkyldioxanes	H_2O	weight	molar			isoprene + trans-piperylene	butylenes + cis-piperylene	unsaturated alcohols	carbon		
0.27	0.31	1 : 1.18	1 : 7.6	2.23	64.0	53.2	10.8	3.1	4.9	83.0	60.2
0.29	0.63	1 : 2.16	1 : 13.9	1.17	75.5	61.6	13.9	2.3	3.3	81.6	73.2
0.23	0.66	1 : 2.86	1 : 18.4	0.83	77.5	62.3	15.2	1.7	2.5	80.5	85.8
0.30	1.22	1 : 4.05	1 : 26.0	0.62	67.5	53.0	14.5	4.6	1.9	79.5	88.0
0.30	1.51	1 : 5.03	1 : 32.4	0.50	69.3	54.3	15.0	4.3	1.7	78.5	93.5
0.30	2.43	1 : 7.97	1 : 51.5	0.32	72.7	58.6	14.1	5.0	0.7	80.6	90.2

The extent of cracking of alkyldioxanes (I) and (II) to olefins (n-butylenes) in this case was considerably greater than in the butadiene and isoprene processes [1]. It represented 16-19% of the alkyldioxanes decomposed, instead of the 4.5-6% reported previously. In this process the reaction products also contained a considerable amount of the aldehyde 2-methylbutanal (IV)—up to 9.5% of the alkyldioxanes (I) and (II) decomposed. In processes described previously the aldehyde content of the reaction products was very small. Thus, the selectivity of the catalytic cleavage of alkyldioxanes (I) and (II) to dienes was found to be considerably less than in the processes described previously.

The effect of steam dilution of the alkyldioxanes is shown in Table 1, from which it can be seen that the reaction rate increased with an increase in the dilution This follows from the facts given, indicating that with an increase in dilution, the contact time falls considerably while the dioxane conversion to unsaturated hydrocarbons remains practically constant. The selectivity of the process (determined by the diene content of the unsaturated hydrocarbons of the contact gas) remained constant over a wide range of dilutions. The carbon deposition on the catalyst and formaldehyde loss (separated during alkyldioxane cleavage) decreased considerably with an increase in steam dilution.

Experiments with different catalyst-operation times showed the advantage of continuous operation for up to 4 hours, followed by catalyst regeneration with a steam-air mixture for 1 hour. The stability of the catalyst was checked over the 4 hours and was found to be satisfactory.

Balance experiments. In order to evaluate the experimental results more accurately, we carried out a series of balance experiments in which all the reaction products were accounted for as accurately as possible. A typical material balance for the catalytic cleavage of a mixture of alkyldioxanes (I) and (II) is shown in Table 2.

The diene fraction, containing a certain amount of n-butylenes, obtained in the balance experiment was further distilled on a laboratory column of 35 theoretical plates (Fig. 3) and the fractions collected were then analyzed for olefin and diene contents. This made it possible to determine quite accurately the isoprene and piperylene (cis and trans isomers) content. This ratio of dienes (37.3% of piperylene and 62.7% of isoprene) was found to be quite close to the ratio of 1-butene and 2-butene in the starting fraction of n-butylenes used for the synthesis of the mixture of isomeric alkyldioxanes (I) and (II). It is known that an equilibrium mixture of n-butylenes at 600° (dehydrogenation temperature of n-butane) contains 33% of 1-butene and 67% of 2-butene [3].

The formaldehyde formed by the reaction remained in the condensate in the form of a dilute (5-6%) formalin solution. The latter may be returned to the process (for condensation with n-butylenes) in the form of a standard 37% solution by concentration under pressure [4].

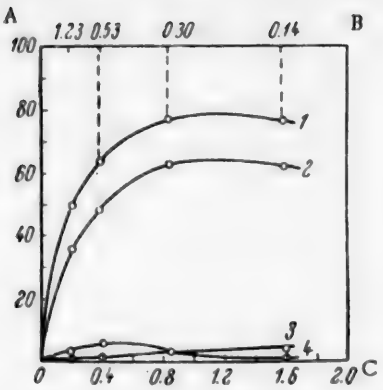


Fig. 1. Catalytic cleavage of a mixture of alkyldioxanes (I) and (II) on "KSD" catalyst at 375° with steam dilution of 1 : 3 by weight. A) Yield on mixture of alkyldioxanes (I) and (II) passed (in mol. %); B) input space velocity of mixtures of alkyldioxanes (I) and (II) (in ml/ml·cat·hr); C) arbitrary contact time (in sec). 1) Alkyldioxane conversion to unsaturated hydrocarbons; 2) isoprene and trans-piperylene yield; 3) alkyldioxanes converted to carbon; 4) unsaturated alcohol yield.

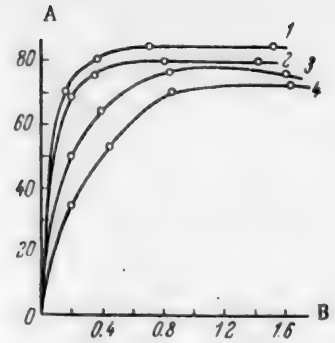
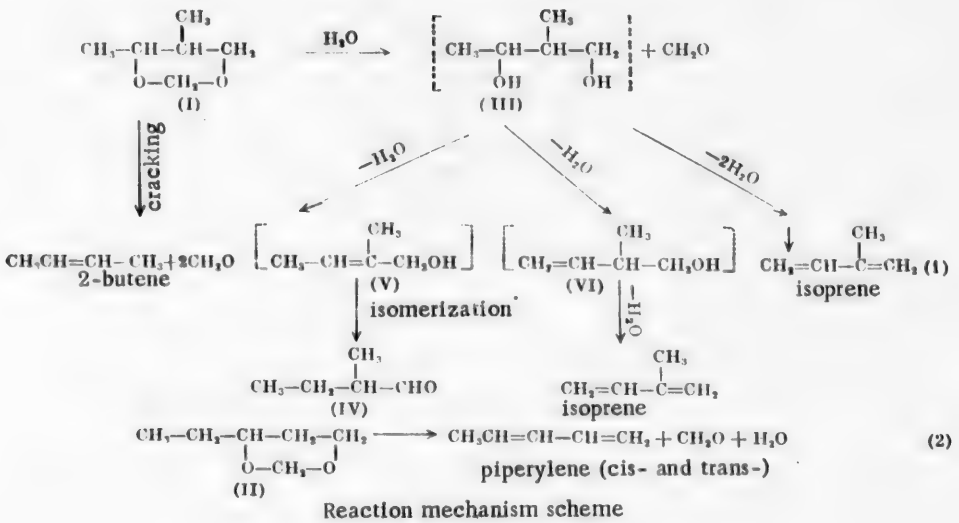


Fig. 2. Conversion of a mixture of alkyldioxanes (I) and (II) to unsaturated hydrocarbons at various temperatures. A) Conversion of mixture of alkyldioxanes (I) and (II) to unsaturated hydrocarbons (in mol. %); B) arbitrary contact time (in sec.). Temperature (in °C): 1) 450, 2) 425, 3) 375, 4) 350.

The reaction mechanism seemed to us to have the following form according to the experimental data given [it is illustrated in detail for 4,5-dimethyl-1,3-dioxane (I)]:



Reaction mechanism scheme

The increase in the reaction rate with an increase in the steam concentration appears to indicate that water participates in the reaction, producing hydrolysis of the alkyldioxane (I). The first stage of the reaction is hydrolysis of (I) to the diol: 2-methyl-1,3-butanediol (III). Product (III) is adsorbed on the catalyst and is dehydrated at a greater rate than the rate of its possible desorption and liberation into the gas phase; therefore it is not found in the reaction products. Dehydration of (III) proceeds with the elimination of two or one water molecules with conversion to isoprene and the unsaturated alcohols (V) and (VI), respectively (these alcohols were detected by analysis, but were not identified).

The β-unsaturated alcohol (V) is isomerized on the catalyst (which has an acid function) to 2-methylbutanal (IV). Isomerization of β-unsaturated alcohols to aldehydes under the action of acidic catalysts was

TABLE 2

Material Balance of the Catalytic Conversion of a Mixture of Alkyldioxanes (I) and (II) over a "KSD" Catalyst. [Temperature 425°, input space velocity of alkyldioxanes (I) and (II) 0.63 ml/ml·cat·hr, alkyldioxane dilution with water 1 : 3 by weight, catalysis time 4 hours; 143.6 g (1.24 mole) of alkyldioxane mixture was passed during the experiment and 124.2 g (1.07 mole) reacted].

Product	Amount obtained		Yield on alkyldioxanes (in mol. %)	
	in g	in moles	passed	decomposed
Isoprene	29.8	0.438	35.3 } 56.3	41.0 } 65.3
Piperylene	17.7	0.260	21.0 }	24.3 }
Butylene	11.1	0.198	16.0	18.6
Undecomposed alkyldioxanes (I) and (II)	16.1	0.139	11.2	—
Unsaturated alcohols*	3.3	0.039	3.1	—
2-Methylbutanal (IV)	8.7	0.101	8.2	9.5
Carbon on catalyst	0.7	0.058	0.8	0.9
Unaccounted losses	—	—	4.4	5.7

The formaldehyde yield was 28.7 weight % on the dioxanes decomposed.

*The unsaturated alcohols were taken to be equivalent to the alkyldioxanes.

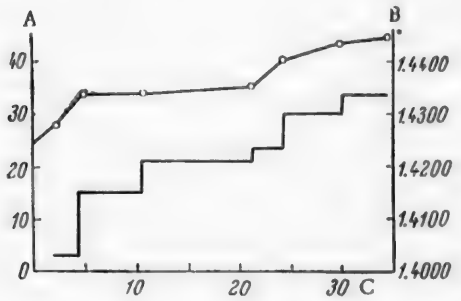


Fig. 3. Graph of distillation of the diene fraction on a laboratory column of 35 theoretical plates. A) Temperature (in °C); B) refractive index(n_D^{20}); C) weight of fraction (in g).

described in [5]. The unsaturated alcohol (VI) is subsequently dehydrated to isoprene, as is indicated by the maximum on the kinetic curve of the dependence of the yield of (VI) on contact time (Fig. 1).

The reaction of 4-ethyl-1,3-dioxane (II) to form piperylene by cleavage proceeds similarly.

EXPERIMENTAL

The laboratory apparatus on which the experiments were performed and the working procedure were described previously [1] The catalytic process parameters and the method of evaluating the experimental results were described in the same place.

The catalyst, the standard one for catalytic conversion of alkyldioxanes into dienes ("KSD"), was a mixture of calcium phosphates.

Isomeric dioxanes. The mixture of 4, 5-dimethyl-1,3-dioxane (I) and 4-ethyl-1,3-dioxane (II) was obtained by reaction of an n-butylene fraction containing 69.5% of 2-butene and 30.5% of 1-butene (determined by infrared spectroscopy), with 37% formaldehyde solution, containing 3% of H_2SO_4. The reaction was carried out in a BAZhM alloy autoclave at 120°; in 3 hours the formaldehyde conversion reached 89.7%. The yield of dioxane mixture was 90% on the formaldehyde converted.

The mixture of dioxanes used for the present experiments had the following characteristics: b p. 133-135° n_D^{20} 1.4220, d_4^{20} 0.9583. The dioxane content was 99.7% and the content of unsaturated alcohols was 0.3%. The separation of (I) and (II) was impossible due to the extreme similarity of their physical properties.

Analysis methods. Experiments for studying the conditions of catalytic cleavage of alkyldioxanes were evaluated in the following way: the total content of unsaturated hydrocarbons in the gas obtained after blowing through the catalyzate heated to 45° was determined by absorption in 84% H_2SO_4 on an Orsat apparatus. The

diene content (isoprene + trans-piperylene) was determined by absorption by maleic anhydride on a Bushmarin apparatus. Under these conditions cis-piperylene does not react appreciably with maleic anhydride [6]. The difference between the total content of unsaturated hydrocarbons in the gas and the diene content, determined on the Bushmarin apparatus, was taken as the content of n-butylenes and cis-piperylene. Thus the yield of dienes was low by the cis-piperylene yield and the yield of n-butylenes was correspondingly high. The unsaturated alcohol content of the condensate after evaporation of the hydrocarbons was determined by the bromide-bromate method. The amount of "carbon" on the catalyst was determined from the weight of carbon dioxide in the regeneration gases (from the increase in weight of ascarite absorption tubes).

Balance experiments. In balance experiments, the catalysis products from several experiments under identical conditions were collected together. The gas collected from these experiments was analyzed as above. The condensate from all the experiments was distilled on a column of 45 theoretical plates; the emergent was also collected in a gasometer and analyzed as above. A series of fractions were collected in the distillation. The fraction with b.p. 24-50°, which contained practically all the diene hydrocarbons, was redistilled with a high reflux ratio to determine the ratio between isoprene and piperylene (Fig. 3). The fraction with b.p. 50-80° contained the whole of the methylbutanol (IV), which distilled as an azeotrope; the content was determined by the hydroxylamine method.

The fraction with b.p. 80-96° was a two-layer liquid. Both layers were analyzed for formaldehyde (with hydroxylamine), unsaturated alcohols (bromide-bromate method), and alkyldioxanes (by hydrolysis in the presence of hydroxylamine hydrochloride [7]). After this fraction had been collected, water containing 4-5% of formaldehyde remained in the distillation flask.

Identification of Reaction Products

Isoprene was isolated by redistillation of the diene fraction of the condensate; it had b.p. 33.5-34.5°, n_D^{20} 1.4202; the adduct with maleic anhydride had m.p. 63.4-63.6° (from benzene); 0.1217 g of substance—81 ml of hydrogen (normal conditions).

Found: hydrogen number 668.
C_5H_8. Calculated: hydrogen number 660.

Literature data [8]: b.p. 34°, n_D^{20} 1.4216; m.p. of adduct 63-64°.

Piperylene. In the distillation of the dienes, the piperylene fraction distilled at 40-44°. It was redistilled to give two fractions: I (mainly the trans isomer) with b.p. 41-42°, n_D^{20} 1.4301 and II (mainly the cis isomer) with b.p. 43.7-44.5°, n_D^{20} 1.4330; 0.1241 g (total fraction)—83.2 ml of hydrogen (normal conditions); the adduct with maleic anhydride (fraction I) had m.p. 58.5° (from benzene); a mixed melting point with the adduct of authentic piperylene (from the Synthetic Rubber Plant) was not depressed.

Found: hydrogen number 670.
C_5H_8. Calculated: hydrogen number 660.

Literature data [9]: trans isomer, b.p. 41.7°, n_D^{20} 1.4300; cis isomer, b.p. 43.8°, n_D^{20} 1.4360; m.p. of adduct (for trans isomer) 58.5°; the cis isomer reacts with maleic anhydride very slowly [5].

2-Methylbutanal (IV). The catalyzate fraction with b.p. 50-80° (upper layer after salting out) was dried and redistilled; a sharp fraction of (IV) was obtained: b.p. 90-91°, d_4^{20} 0.8211, n_D^{20} 1.3945; MR_D 25.01, calculated 25.20; the product (IV) gives an azeotrope with water with b.p. 77°; the (IV) content of the azeotrope is 88%.

Found %: C 69.71, H 11.66.
$C_5H_{10}O$. Calculated %: C 69.70, H 11.58.

2,4-Dinitrophenylhydrazone: m.p. 127° (from alcohol).

Found %: N 21.54
$C_{11}H_{14}N_4$. Calculated %: N 21.05

Reduction of (IV) to alcohol (2-methylbutanol-1). 56 g of (IV) and 20 g of aluminum ethylate in 130 g of absolute ethyl alcohol were heated in a flask with a reflux condenser for 4 hours and then distilled. We collected 40 g of product with the constants: b.p. 131-132°, d_4^{20} 0.8222, n_D^{20} 1.4090; MR_D 26.45, calculated 26.80.

Found %: OH 18.0
Calculated %: OH 19.3.

Unsaturated alcohols. Distillation of the fraction of aqueous condensate with b.p. 50-98° (azeotropes) after drying yielded fractions with b.p. 108-115° and 115-125°, which were shown to contain 67.0 and 55.3% of unsaturated alcohols by the hydroxyl group content and determination of the unsaturated alcohols by the bromide-bromate method. These fractions were not investigated further.

SUMMARY

1. By catalytic cleavage of alkyldioxanes, obtained by reacting n-butylenes with formaldehyde, it is possible to synthesize simultaneously isoprene and piperylene in a ratio which corresponds approximately to the 1-butene and 2-butene contents of the n-butylene fraction.

2. We studied the process conditions, which give a diene yield of 65 mol. % on the alkyldioxanes decomposed.

3. The process studied had a lower selectivity than the analogous processes based on propylene and isobutylene. The main side reactions are cracking of alkyldioxanes to form n-butylenes (16-19 mol. %) and the formation of the aldehyde 2-methylbutanal (9-10%). The latter may be reduced to the corresponding alcohol.

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BRIEF COMMUNICATIONS

SOLUTION OF ALUMINA IN FELDSPAR MELTS

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In recent years investigators have frequently turned to alumina as a material for increasing the mechanical strength of ceramics. Some authors have explained the improvement in properties thus produced by the introduction of a component (alumina) with a high modulus of elasticity, strengthening of the glass phase due to solution of alumina, and crystallization of mullite [1, 2]. The literature contains limited data on the study of the crystalline phases of porcelain with the replacement of quartz by alumina in the latter [1]. However, there have been no investigations at all of the kinetics of alumina solution in feldspar.

As glass has high brittleness and low mechanical strength, the introduction into its composition of oxides with a high modulus of elasticity should improve its mechanical properties.

The purpose of our investigation was to determine the effect of the solution of alumina in feldspar on the microhardness, microbrittleness, and elastic properties of the glass phase formed.

Samples for the investigation were prepared from a mixture of potash feldspar, and alumina by moist pressing at 1000 kg/cm^2 and a moisture content of 7-8% in the form of discs, 20 mm in diameter and 3 mm thick. The composition of the potash feldspar (in %) was: SiO_2 66.64, $Al_2O_3 + TiO_2$ 18.53, Te_2O_3 0.27, CaO 0.72, MgO 0.09, K_2O 9.65, Na_2O 3.22; the loss on firing was 0.72. The alumina was first fired at 1600° and powdered on a vibromill with subsequent washing in 20% hydrochloric acid. The extent to which iron was washed out was checked by chemical analysis. The compositions of the mixtures investigated are given in Table 1.

TABLE 1

Mixture composition

Mixture No.	Feldspar (in %)	Alumina (in %)
1	95	5
2	90	10
3	85	15
4	80	20
5	75	25

The samples were fired in a Silit furnace at 1200, 1300, 1350, 1450, 1500, and 1600° and kept at these temperatures for 1 and 6 hours with the temperature raised at 200° per hour.

The main investigation methods were x-ray structural quantitative analysis from the ionization curves on a Giprotsement apparatus [3], determination of the microhardness and microbrittleness on a PMT-3 apparatus [4-6], and microscopic investigations of polished sections with an MIM-8 metallographic microscope and of transparent sections with a polarization microscope.

TABLE 2

X-ray Analysis Data

Given alumina content (in %)	Alumina content (in %) after firing					
	1200°		1300°		1350°	
	firing time (in hrs)					
	1	6	1	6	1	6
5	4.5	4.3	4.25	3.75	3	1
10	9	8	7.25	5.75	6.5	4.25
15	14.5	13.75	13.75	10.85	9	5.75
20	20.5	17.75	16.6	14.2	15	11.5
25	25	22	22	17.75	17.75	15

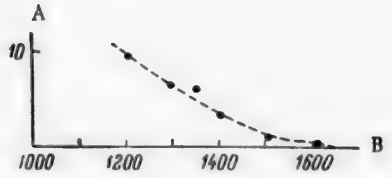

Fig. 1. Effect of firing temperature on the solution of alumina in feldspar (Al_2O_3-10%). A) Alumina residue (in %), B) firing temperature (in °C).

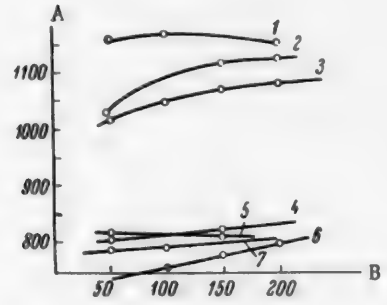

Fig. 2. Change in microhardness of glass phase relative to the depth of impression of the pyramid. Firing temperature 1300°, firing time 1 hr. A) Load on pyramid (in g); B) impressions with cracks (in %). Al_2O_3 content (in %): 1) 25, 2) 20, 3) 15, 4) 10, 5) glass phase, 6) 10% quartz, 7) 5% quartz.

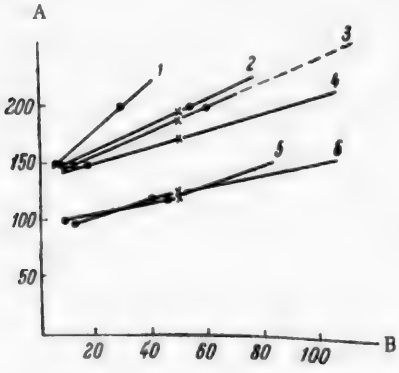

Fig. 3. Change in microbrittleness of glass phase relative to composition. A) Load on pyramid (in g), B) impressions (in %). Al_2O_3 content (in %): 1) 20, 2) 15, 3) 10, 4) 5, 5) 10% SiO_2, 6) glass phase.

The amount of undissolved alumina was determined by x-ray analysis on powders (passing through a sieve with 10,000 holes/cm^2) with an internal standard in the form of chemically pure calcium fluoride. The calculation method was given in a previous article [7].

The results of investigations for three firing temperatures are given in Table 2.

The relation of alumina solution to firing temperature for a composition containing 10% of alumina is shown in Fig. 1.

For the determination of microhardness and microbrittleness polished samples were prepared for all five mixtures and the two firing temperatures of 1300 and 1500° (firing time 1 hr).

Strictly identical conditions were used for polishing the samples to decrease the scatter of the readings due to to nonidentical sample surfaces.

TABLE 3

Results of Microscopic Investigation of Transparent Sections

Mixture composition		Firing temperature (in °C)					
alumina (in %)	feldspar (in %)	1200	1300	1350	1400	1500	1600
5	95	Acute angled grains of alumina which did not fuse. Cementation of glass phase. Fields of submicroscopic mullite observed at an Al_2O_3 content of 20-25%.	Alumina grains slightly fused. Finely crystalline mullite seen at an Al_2O_3 content of 20-25%.	Fusion of corundum grains increased. Thickness of fusion layer 1-2 μ and mullite readily visible at an Al_2O_3 content of 20-25%.	Fusion layers 2-3 μ. Mullite in the form of clearly expressed coarse crystals at an Al_2O_3 content of 15%.	Traces of corundum remained. Mullite well expressed at an Al_2O_3 content of 10%.	Corundum completely fused. Melt homogeneous. No mullite.
10	90						
15	85						
20	80						
25	75						

The microhardness was calculated from the formula

$$H = 1854 \frac{P}{d^2} \text{ (kg/mm}^2\text{)}$$

where P is the load (in g) and d the size of the diagonal of the impression (in μ).

For each sample the microhardness was determined for 50 impressions with measurement of two diagonals and the size of each diagonal determined three times. The nature of the impression and the position of the impression (on alumina grains or on the glass-phase surface) were recorded in detail in the laboratory notebooks.

The microbrittleness was determined with loads of 50, 100, 150, and 200 g. It was determined as the percentage of the total number of impressions with cracks [6]. The nature of the change in microhardness and microbrittleness for different depths of the impression from the pyramid of the apparatus is shown in Figs. 2 and 3.

The data presented above make it possible to draw the following conclusions. The solution of alumina in a feldspar melt begins practically at 1200° or slightly lower. Due to the high strength and chemical stability of corundum the solution of alumina, in contrast to that of quartz, proceeds very slowly. Complete solution of 20% alumina in feldspar is observed only at 1600°. At the lower temperatures of 1400 and 1500°, examination of clear sections reveals the presence of two crystalline phases: alumina and mullite (Table 3).

Ionization curves (Fig. 4) confirmed the microstructural analysis data. X-ray patterns obtained by the Debye powder method did not show the presence of mullite even with 25% Al_2O_3. As all the material presented above shows, when the temperature was raised from 1200 to 1350°, the percentage solubility of Al_2O_3 increased from one at 1200° to forty at 1350°. Increasing the firing time from 1 hour to 6 hours at 1300° increased the solution from 10 to 40%.

Data on microhardness and microbrittleness lead to the following conclusions: Alumina itself has a high microhardness and at low temperatures when fusion of the grains is minimal, the increase in microhardness is connected with the high strength of corundum itself. When the corundum passes into the melt, the glass phase is strengthened dur to fusion of the alumina. As in the solution of quartz, microsections show the formation of diffusion layers with a higher refractive index. With an increase in the firing temperature and the firing time at the

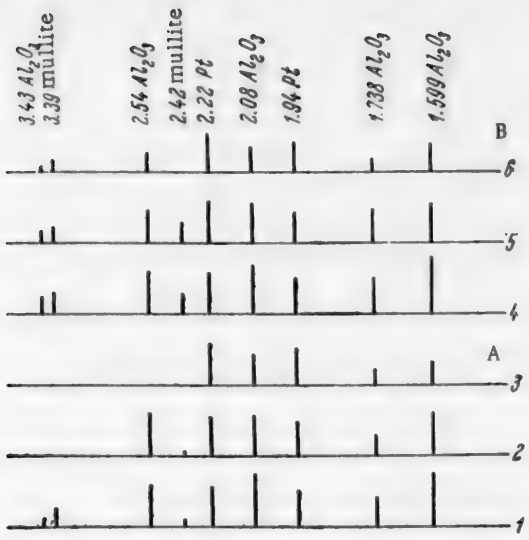

Fig. 4. X-ray patterns of Al_2O_3 solution in a feldspar melt at different temperatures. A) Firing temperature 1400°, firing time 1 hr , B) firing temperature 1500°, firing time 1 hr. Al_2O_3 content (in %): 1) 25, 2) 20, 3) 15, 4) 25, 5) 20, 6) 15.

final temperature, the thickness of the diffusion layers increases, the alumina grains gradually fuse, and the microhardness of the glass phase increases correspondingly, while its microbrittleness falls.

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APPLICATION OF THE ARSENIC-SODA METHOD TO THE PURIFICATION OF GASES WITH A HIGH CARBON DIOXIDE CONTENT

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A number of industrial gases contain, in addition to hydrogen sulfide, large amounts of carbon dioxide, which may reach 25% and more. In recent years the arsenic-soda method has been developed considerably for freeing gases from H_2S. As the experimental operation of a number of plants has shown, this method makes it possible to extract H_2S selectively with the formation of commercial sulfur; carbon dioxide remained almost completely in the gas. However, the presence of large amounts of CO_2 in the gas could reduce the pH of the arsenic-soda solutions and this could lead to the precipitation of arsenic sulfide from the working solution.

Up to the present time the arsenic-soda method has been used for purifying gases containing not more than 20% CO_2. Therefore, it was interesting to check the possibility of using it for purifying gases with a higher CO_2 content.

Experiments were carried out with gases containing 30 and 15 vol. % CO_2 on an apparatus whose plan is illustrated in the figure. The gas containing 15 vol. % CO_2 was chosen for comparison purposes. The gas to be purified, containing 15% carbon dioxide, also contained 82% propane-propylene and 3% hydrogen sulfide. The gas containing 30% carbon dioxide also contained 67% propane-propylene and 2.6% hydrogen sulfide.

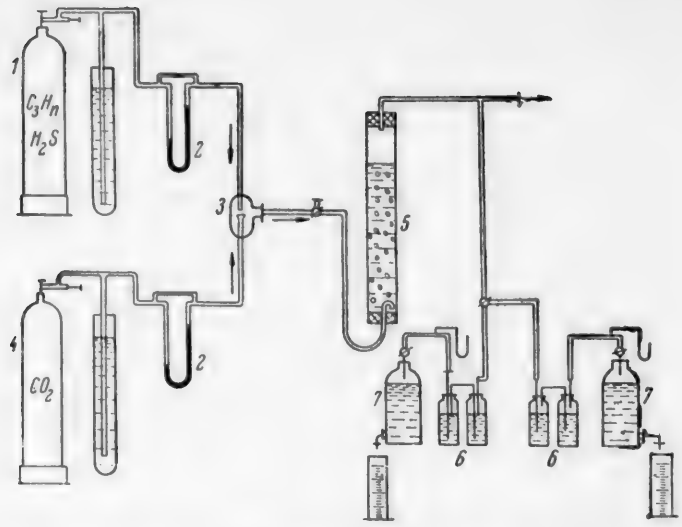
The propane-propylene fraction was passed from tank 1, through rheometer 2 into the mixture 3, which was supplied with carbon dioxide from tank 4, through rheometer 2. The gas mixture was freed from H_2S in absorption column 5, into which was poured a 0.1 M solution of Na_2HAsS_3O. Part of the purified gas was taken for analysis into bubblers 6. The amount of gas going to analysis and passing through the bubblers was measured in bottles 7. An experiment lasted for one hour and samples taken consecutively for analysis showed practically identical degrees of purification. The average percent purification is given in the table.

The data obtained, which are presented in the table, indicate that the degrees of purification and also the rates of purification of gases containing 15 and 30% CO_2 were similar to each other. The degree of removal of H_2S from gases containing 15% CO_2 was 75-85% and from gases containing 30% CO_2, 79-85%.

In parallel with experiments to study the degree of purification, an investigation was made of the stability of the arsenic-soda solution during purification of gases containing 30% CO_2. Experiments with 0.1 M Na_2HAsS_3O solution showed that the solution was quite stable both during the actual purification of the gas containing 15% CO_2 and also during subsequent saturation of the spent solution with gases free from H_2S, but containing 15 and 20% CO_2. In the purification of gases containing 30% CO_2, the solution was not decomposed during the experiment either.

Decomposition of the solution with the precipitation of arsenic sulfide began when the spent solution was subsequently saturated for 1 hour with gas free from H_2S, but containing 30-35% CO_2. A similar phenomenon could be observed when the spent solution was allowed to stand, even without gases passed through it.

In connection with the results obtained it was interesting to investigate the stability of arsenic-soda solutions with a somewhat higher pH value during the purification of gases containing 30% CO_2. For this purpose we prepared solutions in which the Na : As ratio was 2.5 : 1 and not 2 : 1 as in the experiments described above. In an investigation of this solution we observed no decomposition of sodium thioarsenate either in the purification



Plan of apparatus for freeing gases from hydrogen sulfide with arsenic-soda solution. 1) Tank of propane-propylene fraction; 2) rheometers; 3) mixer; 4) carbon dioxide tank; 5) column with arsenic-soda solution; 6) bubblers; 7) bottles.

Removal of Hydrogen Sulfide from Gas with Arsenic-Soda Solution

Expt. No.	Solution composition	Solution concentration	Gas composition (vol. %) before purification			Gas composition (vol. %) after purification		Degree of purification (in %)
			H_2S	CO_2	C_nH_m	H_2S	$CO_2+C_nH_m$	
1	Na_2HAsS_3O	0.1	3.0	15.0	72.0	0.39	99.61	87
2			3.0	15.0	72.0	0.79	99.21	74
3			2.6	30.4	67.0	0.39	99.61	85
4			2.6	30.4	67.0	0.54	99.46	79
5	$Na_{2.5}H_{0.5}AsS_3O$	0.1	2.6	30.4	67.0	0.58	99.42	76
6			3.0	15.0	72.0	0.59	99.41	80

of gases containing 15% CO_2 or of gases containing 30% CO_2. However, when the spent solutions were allowed to stand for 3 hours, the solution saturated with gas containing 30% CO_2 became turbid due to the precipitation of arsenic sulfide.

The investigation of the stability of solutions when gas containing 30% CO_2, but free from H_2S, was passed through them was connected with the fact that under industrial conditions, in the upper part of the scrubber the absorbent is in contact with gas that has already been freed from H_2S in the lower layer of the scrubber.

Thus, as a result of these experiments we can conclude that arsenic-soda solution can be used for purification of gases containing up to 30% CO_2, but the composition of the solution should be somewhat different from that for gases containing 15% CO_2. In this case the ratio of soda to arsenic should be somewhat higher.

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VISCOSITY OF MELTS OF THE BINARY SYSTEMS $NaF-MgF_2$ and $Na_3AlF_6-NaMgF_3$

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It has long been the practice to introduce magnesium fluoride into the electrolytes of aluminum baths to raise the technical economic indices of the electrolysis [1, 2], but the physicochemical properties of electrolytes with the additive have not yet been studied sufficiently.

According to the melting-point diagram [3], the binary system $NaF-MgF_2$ contains the congruent chemical compound $NaMgF_3$. First of all, it seemed interesting to determine the behavior of this chemical compound on fusion, i.e., to obtain information on the stability of the corresponding complexes in the liquid phase. For this purpose the viscosity of melts of the binary system $NaF-MgF_2$ was investigated.

In addition, a study of the viscosity of the binary system $Na_3AlF_6-NaMgF_3$ was of importance for the purposes of practical aluminum electrolysis.

The viscosity was measured with a torsion balance viscometer. The apparatus and experimental and calculation procedures• were described in detail previously [3].

The starting materials were "pure" grade sodium and magnesium fluorides and sublimed aluminum fluoride.

Binary system $NaF-MgF_2$. In the case of this binary system we studied the temperature dependence of viscosity for 10 melts over the range of MgF_2 concentrations from 0 to 80 mol. %. Melts with a higher MgF_2 content could not be investigated due to their high melting points. The experimental data are presented in Table 1.

These data were used to draw viscosity polytherms, from which were constructed the isotherms illustrated in Fig. 1. The same figure also shows the melting-point diagram and the viscous flow activation energy, calculated from Frenkel's formula [4].

As can be seen, the viscosity increased with an increase in the magnesium fluoride concentration. The isotherms showed an appreciable inflection above the chemical compound $NaMgF_3$. Their sigmoid form was typical of systems with chemical interaction of the components. The presence of complexes in the melt was indicated similarly by a maximum on the activation-energy curve.

As regards the structure of the melts, they may be regarded as ionic liquids. Sodium fluoride is a typical heteropolar compound and magnesium fluoride is the same, though it also contains covalent bonds. Mixing yielded melts consisting of Na^+, Mg^{2+}, and F^- ions, arranged in close order. When the composition was close to equimolecular, there arose in the melt temporarily ordered groupings of ions—complex anions.

As regards the nature of the complex former, in the past the opinion was put forward [5] that it was Na^+, giving NaF_3^{2-} anions. However, this opinion contradicts contemporary ideas on the structure of molten salts and, in particular, crystallochemistry.

Actually, according to Pauling, the radii of Mg^{2+} and Na^+ ions are 0.65 A and 0.95 A, respectively. Their generalized moments, characterizing the strengths of the electrical fields of the ions, are in the ratio

•The densities of the melts required for the calculation were taken from the data of A. A. Kostryukov and V. P. Bodrov.

TABLE 1

Temperature Dependence of the Viscosity of Melts of the System $NaF-MgF_2$

Melt No.	MgF_2 content (in mol. %)	Temp. (in °C)	Viscosity (in centipoises	Melt. No.	MgF_2 content (in mol. %)	Temp. (in °C)	Viscosity (in centipoises
1	0	1015	1.54	6	40	1025	2.90
		1068	1.24			1085	2.40
		1115	1.11			1173	2.05
		1160	1.05			1215	1.87
2	10	1040	1.60	7	50	1037	3.28
		1080	1.48			1057	2.98
		1135	1.36			1080	2.79
		1170	1.28			1170	2.50
						1225	2.29
3	20	882	3.13	8	60	1015	4.19
		937	2.53			1088	3.38
		985	2.07			1130	3.02
		1065	1.88			1173	2.72
		1100	1.51			1215	2.51
						1243	2.40
4	22.5	905	3.00	9	70	1077	3.68
		944	2.64			1120	3.40
		986	2.36			1165	3.00
		1017	2.16			1200	2.76
		1095	1.80			1227	2.62
		1145	1.62				
5	30	935	2.90	10	80	1190	3.24
		1000	2.49			1228	2.94
		1062	2.16			1272	2.78
		1167	1.76			1323	2.54
		1206	1.54				

TABLE 2

Temperature Dependence of the Viscosity of Melts of the System $Na_3AlF_6-NaMgF_3$

Melt No.	$NaMgF_3$ content (in mol. %)	Temp. (in °C)	Viscosity (in centipoises)
11	0	1027	2.23
		1053	2.06
		1120	1.65
		1165	1.50
		1225	1.32
12	35.3	1018	2.42
		1080	1.98
		1130	1.72
		1183	1.50
13	56.8	1068	2.35
		1110	2.01
		1183	1.72
		1215	1.50
14	75	1013	2.85
		1067	2.51
		1130	2.17
		1165	1.95
		1210	1.75
15	89	1027	2.97
		1080	2.51
		1130	2.35
		1192	1.92

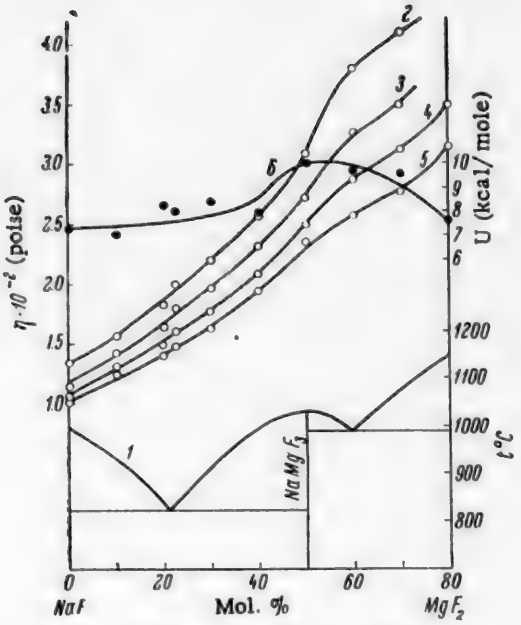

Fig. 1. Properties of melts of the binary system $NaF-MgF_2$. 1) Melting-point diagram [8]; viscosity isotherms at the following temperatures (in °C): 2) 1050; 3) 1100; 4) 1150; 5) 1200; 6) viscous flow activation energy.

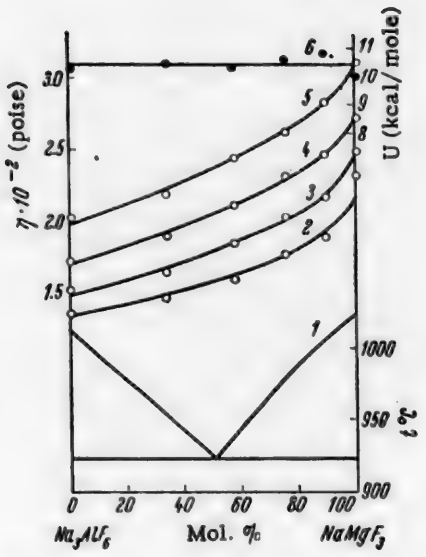

Fig. 2. Properties of melts of the binary system $Na_3AlF_6-NaMgF_3$. 1) Melting-point diagram [8]; viscosity isotherms at the temperatures (in °C): 2) 1200; 3) 1150; 4) 1100; 5) 1050; 6) viscous flow activation energy.

1 : 0.23. Hence it follows that the melt contains the complex ions MgF_3^- and not NaF_3^{2-}. This is also indicated by the ratio of the energies of formation of the complex ions, calculated by the formula presented in A. A. Grinberg's book [6], as this energy is found to be a factor of 3.7 greater for the ion MgF_3^- than for NaF_3^{2-}.

It is interesting to compare the system examined with two others: $NaF-CaF_2$ and $NaF-AlF_3$. Complex formation does not occur in the first of these [7].

The second system has a stable compound, cryolite. The complex anions corresponding to it, AlF_6^{3+}, are more stable than MgF_3^-, which is confirmed by a clearer dystectic on the melting-point diagram and sharper maxima on the viscosity and density isotherms [3] and is explained by the ratio of the radii of Al^{3+} and Na^+ ions (1 : 1.9) and their generalized moments (1 : 0.09).

Binary system $Na_3AlF_6-NaMgF_3$. In the case of this system we studied the temperature dependence of viscosity for five melts (Table 2).

The isotherms constructed from these data had a monotonic form (Fig. 2), indicating the absence of interaction of the system components. This was also indicated by the constancy of the viscous flow activation energy.

From the point of view of aluminum electrolysis, it is important to note that magnesium fluoride, introduced into the electrolyte in up to 6 weight %, is evidently completely bound in the compound $NaMgF_3$. Thus, the activity of Mg^{2+} cations is reduced, promoting the displacement of their discharge potential to the more negative side. Apparently, as a result of this, hardly any magnesium is liberated together with aluminum, though their electrode potentials are quite close and magnesium dissolves readily in liquid aluminum.

SUMMARY

By a study of the viscosity of melts of the binary systems $NaF-MgF_2$ and $Na_3AlF_6-NaMgF_3$, which are important in the theory and practice of the electrolytic production of aluminum, it was shown that the form of the viscosity isotherms and the activation-energy curve for the binary system $NaF-MgF_2$ confirms the existence in the molten state of the chemical compound $NaMgF_3$, which was previously detected by thermal analysis. Some ideas are put forward on the structure of melts corresponding to this complex compound.

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NEW METHOD OF PREPARING HOMOGENEOUS FERROMAGNETIC POWDERS WITH A HIGH DEGREE OF DISPERSION

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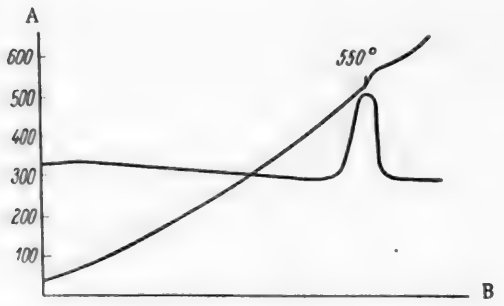
Contemporary technology, especially radio technology, requires finely dispersed ferromagnetic powders. However, comparatively little is known of such powders satisfying technical requirements. They include iron carbonyl, ferrocarts, and special magnetic powders based on iron, cobalt, etc. All these powdered materials are obtained as a result of complex technical processes and they are for the most part inhomogeneous as regards particle size, so that high-quality and homogeneous material is expensive. Magnetic powders are prepared in the following way, for example: Finely powdered iron oxide is subjected to prolonged reduction in a stream of hydrogen in special furnaces. Sometimes such powders are obtained by thermal decomposition of ferrous oxalate or iron pentacarbonyl [$FeC_2O_4 \cdot 2H_2O$ and $Fe(CO)_5$]. However, though these powders are fine, they are readily oxidized in air, often pyrophoric, and inconvenient in use. There are ferromagnetic pastes produced by treatment of ferric salts with $[NH_4]_2S_3$ solutions [1]. The black, pasty substance is readily molded and has high magnetic indices, but is very unstable chemically, decomposes when pressed, is pyrophoric, and continually liberates hydrogen sulfide. The average particle size of ferromagnetic powders obtained by these methods reaches 100-150 μ and powders with a grain size of 10 μ are obtained with great difficulty. In the production of ferromagnetic antennas, magnetic circuits of generators with a wide frequency range, and many others there is a pressing need for magnetic powders that are homogeneous as regards grain size and have a particle size of the order of 1 μ and less. The possibility of preparing ferromagnetic powders in an aqueous medium was demonstrated in the work of Katsuray and Fuda [2] and Jamagutchi [3]. Independent of these authors, we observed the formation of a ferromagnetic precipitate from solutions and gave the technology of its formation.



Thermogram of ferromagnetic powder. A) Temperature (in °C); B) time.

We were able to prepare a ferromagnetic powder with a particle size less than 1 μ in the following way: An aqueous solution of a ferrous salt [for example, $FeSO_4 \cdot 7H_2O$ or $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$] was treated with excess 10% NH_4OH solution to a definite smell of ammonia and the reaction mixture boiled in air for about two hours. The paste gradually darkened, changing from a light-blue color to dark green, and then it rapidly acquired a velvety-black color. This marked the end of the reaction.

The finely crystalline precipitate readily settled and the precipitation rate was increased in a magnetic field. The precipitate was washed with water several times by decantation and then separated on a filter and dried at room temperature. In the dry state the substance was a fine, mat-black powder with clearly expressed ferromagnetism.

On analysis of the powder it was found that with firing in air the weight of 100 mg of powder increased to 0.1032 g, i.e., by 3.2%. Theoretically the increase in weight should be 3.4%. Titration with permanganate

showed that the powder contained about 25% of ferrous iron, which agrees well with the theoretically calculated content of 24.15% [by the reaction $2Fe_3O_4 + {}^1/_2\ O_2 \rightarrow 3Fe_2O_3$].

All that has been said above indicated that we were dealing with Fe_3O_4 or $Fe[FeO_2]_2$.

A thermogram was plotted in air and it is shown in the figure.

As the figure shows, there was one exothermal effect. The analysis showed that Fe_2O_3 was formed at 530°.

A ferromagnetic powder may be obtained by using KOH, Na_2CO_3, NH_4OH, etc., as precipitants. Syntheses could start from an aqueous solution of ferric chloride, to which was added rongalite ($NaHSO_2 \cdot H_2CO \cdot 2H_2O$) with slight acidification of the solution with hydrochloric acid. Sufficient rongalite was taken for reduction of 30-35% of the ferric iron to ferrous; instead of reducing part of the ferric iron, it was possible to take a mixture of ferrous and ferric iron in a ratio of 1 : 2. After this, a slight excess of KOH was added to the solution and the reaction mixture heated.

However, the ferromagnetic powder was best precipitated with a 10% solution of NH_4OH and this gave high-quality precipitates.

The chemistry of Fe_3O_4 formation may be explained in the following way: It can be assumed that treatment of a solution of ferrous salts with an alkaline reagent forms complicated and unstable complex compounds, for example, ammoniates when NH_4OH is used and aquohydroxo complexes in the case of KOH or Na_2CO_3; these compounds are gradually decomposed by heating and under the action of atmospheric oxygen. The $Fe(OH)_3$ molecules obtained under these conditions are very active and readily lose a water molecule to form ferric acid: $2Fe(OH)_3 \rightarrow H_2[Fe_2O_4] + 2H_2O$. The hydrogen of this acid is readily replaced by ferrous ions and the salt formed precipitates in the form of a crystalline precipitate. In addition, the excess NH_4OH, which participates in the process, volatilizes from the surface of the heated solution and hinders absorption of atmospheric oxygen by the solution. Prolongation of the formation of the magnetic powder improves its quality, as with a slow process the amount of nonmagnetic $Fe(OH)_3$ and iron oxyhydroxide, which are inert constituents in the precipitate, was found to be minimal.

The ferromagnetism could not be measured accurately as it was found to be considerably higher than the resolving capacity of the available apparatus. In a rough measurement on a molding (pressed at 150 atm), the permeability was found to be close to 5.

Preliminary experiments showed that the magnetic powder can find wide application in the production of magnetites, ferromagnetic tape, and magnetic circuits, in the magnetic detection of defects in steel and iron articles, and in the production of current-carrying devices, replacing graphite, as the ferromagnetic powder has metallic electrical conductivity. In addition, it is used in the lubrication of ground-glass joints of apparatuses containing alkali, replacing graphite; when incorporated in a cellulose nitrate varnish, the powder gives a black, mat paint with good covering power. This paint may be used for painting the inside surfaces of optical equipment.

When the synthesis is carried out in a thoroughly cleaned vessel, a mirror is formed on the surface of the latter, and this conducts an electric current so that the substance can replace aquadag.

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ELECTRODEPOSITED COATING OF ANTIMONY AND ITS PROPERTIES

N. P. Fedot'ev, S. Ya. Grilikhes, and I. B. Naryshkina

As is known, antimony prepared metallurgically is a silvery-white, shiny, friable metal. It does not dissolve in alkalis or hydrochloric or dilute sulfuric acids. These general characteristics apply to electrodeposited coatings, but must be supplemented by information on the protecting power and mechanical properties of antimony deposits. The data in the literature largely concern the preparation of coatings and deal little with their properties.

In this work we investigated the electrode processes during antimony deposition from a citric acid electrolyte and the properties of these coatings.

The antimony was deposited from an electrolyte of the following composition: antimony trioxide 50-55 g/liter, potassium citrate 144 g/liter, and citric acid (total) 139 g/liter. The pH of the solution was 3.5-3.7 [1]. Soluble antimony anodes were used in electrolysis. The antimony was deposited on steel on a copper sublayer.

An investigation of the effect of electrolyte composition and electrolysis conditions on the metal current yield and quality of the coating showed that with a cathode current density up to 0.5 a/dm^2 the current yield depended little on the antimony trioxide concentration over a range of 25-100 g/liter of Sb_2O_3. With a further increase in trioxide concentration, the current yield increased. With an increase in current density there was a decrease in current yield, which was greater the lower the trioxide concentration (Fig. 1). The working range of current densities increased with an increase in the trioxide concentration. With an increase in current density the external appearance of the deposits changed from a mat light gray to a shiny surface. The shiny coatings were cracked. Dense deposits were obtained at an antimony trioxide concentration of 50 g/liter in the solution and current densities of 0.2-2 a/dm^2. Stirring the electrolyte made it possible to raise the current density to 3 a/dm^2. The addition of 1 g/liter of sodium 2,7-naphthalene-disulfonate to the electrolyte gave semishiny, uncracked antimony coatings.

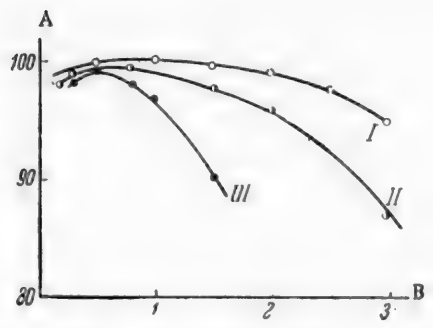

Fig. 1. The effect of current density on cathode current yield at different Sb_2O_3 concentrations in the electrolyte. A) Cathode current yield (in %); B) current density (in a/dm^2). Sb_2O_3 (in g/liter): I) 25, II) 50, III) 100.

An increase in the temperature from 20 to 70° had practically no effect on the current yield, but the external appearance of the deposits deteriorated—they were gray and coarsely crystalline.

Antimony deposition from a citric acid electrolyte was accompanied by very little polarization.

With a current density up to 0.8 a/dm^2 the antimony anode dissolved to give 100% current yield. At current densities above 0.8 a/dm^2 the anode was passivated and a dark, crumbly deposit formed on its surface, oxygen began to be evolved, and the current yield fell (Fig. 2). When the polarizing current was switched off, the passive film dissolved in the electrolyte.

The anode polarization curves plotted for a citric acid electrolyte showed the existence of a limiting current plateau. The addition of sodium 2,7-naphthalene-

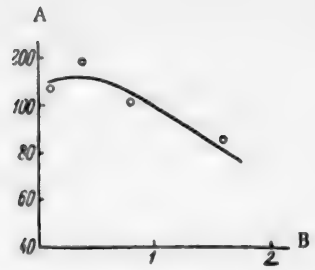

Fig. 2. The effect of current density on anode current yield. A) Anode current yield (in %); B) current density (in a/dm^2).

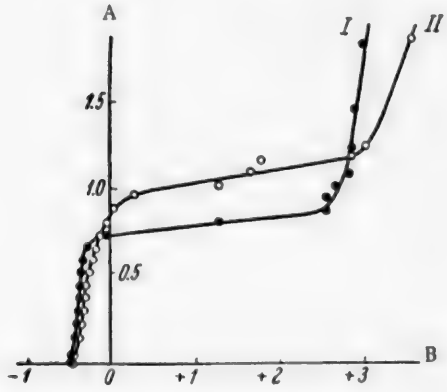

Fig. 3. The effect of current density on the antimony anode potential. A) Current density (in a/dm^2); B) potential (in v). I) Electrolyte without naphthalenedisulfonic acid; II) electrolyte with 1 g/liter of naphthalenedisulfonic acid.

disulfonate to the bath increased the limiting current density somewhat. In the curves in Fig. 3, the potential values are given relative to the hydrogen scale.

A comparison of cathode and anode current yields showed that under working conditions when the anode current density did not exceed 0.8 a/dm^2, they were equal and were approximately 100%.

Antimony coatings obtained under optimal electrolysis conditions were readily polished to a mirror finish. The polished coatings had a bluish tinge and did not darken from handling or prolonged contact with air. In contrast to metallurgical antimony, electrodeposited antimony coatings were not very friable. In a test for strength of adhesion to the base metal by bending a sample covered with an antimony layer 20 μ thick through 180° until the sample broke, no cracking or crumbling of the coating was observed.

Three types of corrosion tests were carried out: in 3% NaCl solution, in a desiccator with 98% relative humidity, and in a heat and moisture chamber under the following conditions: 9 hours at 35° and 98% relative humidity, then for 15 hours at 20-22°, when dew precipitated. The duration of each type of test was 28 days. Nickel coatings were tested at the same time as the antimony coatings. The thickness of the deposits was 20 μ in each case. After the tests in the desiccator and the heat and moisture chamber, no traces of corrosion were observed on the samples covered with antimony. In tests with NaCl solution the antimony coatings lost their shine and a white, friable film of corrosion products formed on them. No corrosion of the base metal was observed in any case. The corrosion resistance and protecting power of the antimony coating differed little from those of the nickel coating.

The microhardness of the antimony deposits was 117 kg/mm^2. The contact resistance with point contact and 100 g pressure was 0.018 Ω and with 10 g pressure, 0.078 Ω.

SUMMARY

1. The cathode and anode current yields during antimony deposition from a citric acid electrolyte under working conditions when the anode current density did not exceed 0.8 a/dm^2 were about 100%. An increase in the anode current density resulted in passivation of the anode and a decrease in the anode current yield.

2. Antimony coatings are similar in protecting power and corrosion resistance to nickel coatings of the same thickness.

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EFFECT OF ALKALI AND ALKALI EARTH METALS ON THE CURRENT YIELD OF ZINC IN THE ELECTROLYSIS OF ALKALINE AND ACID SOLUTIONS

M. D. Zholudev

In an article from our laboratory [1], the hypothesis was put forward that during the electrolytic preparation of zinc from sulfate solutions, the presence of alkali and alkali earth metal ions decreases the current yield of zinc, as at sufficiently high concentrations of these ions in the electrolyte they are discharged simultaneously with zinc ions to form an intermetallic compound on the cathode. In support of this hypothesis the authors gave mainly the values of the cathode potentials which, with sodium ions, for example, present in the solution, were more electropositive at low current densities than in pure zinc solutions and became more electronegative with an increase in current density. The authors considered that the more positive potentials in the presence of sodium indicated the solution of its intermetallic compounds with zinc, while the increase in potential in a negative direction with an increase in current density indicated the phenomenon of "cathodic protection" by these intermetallic compounds.

Literature sources [2, 3] state that zinc gives the compounds $NaZn_4$, $NaZn_{11}$, $NaZn_{12}$ and $NaZn_{13}$ with sodium, but there are no data on the heats of formation of these compounds in the usual handbooks [4-7]. If these compounds exist, their heats of formation should be high and the alloys should be stable.

Lately, in studying the electrolysis of solutions of sodium zincate [8], we reexamined the problem of the effect of alkali metals on the electrodeposition of zinc; such an effect should appear much more strongly in a concentrated sodium hydroxide solution than in acid zinc sulfate solutions; it was considered that the sodium ions would affect the formation of zinc sponge in alkali solutions, especially at low current densities.

In order to check these hypotheses, we measured the current yields of zinc in the electrolysis of zincate solutions containing from 1 N to 12 N free alkali and a constant zinc concentration of 15 g/liter and these were found to be equal and practically 100% in all cases. A qualitative analysis of zinc deposits obtained from zincate and sulfate solutions with sodium ions added (50 g/liter) showed that sodium was absent from the cathodic zinc. The emf of a cell consisting of zinc prepared by electrolysis of pure zinc sulfate solution and zinc prepared from acid and alkaline solutions in the presence of sodium ions equaled zero. In order to avoid the effect on the emf of rapid leaching of sodium from the alloy, the latter was constantly cleaned off with a piece of sharp glass.

These experiments raised doubts about the possibility of the simultaneous deposition of alkali and alkali earth metals and zinc on the cathode. The previous experiments [1] required checking with purer solutions and for longer electrolysis times.

As cathodes we used a rotating disc electrode and a stationary cylinder of TsV grade zinc; at low current densities there was no difference in the hydrogen current yields. Solutions of chemically pure zinc sulfate and sulfuric acid were treated with a direct current of low strength with platinum electrodes for 15 days. The current yield of zinc was determined, as previously [9], by trapping the hydrogen liberated at the cathode to obtain the so-called current yield of hydrogen. We previously described [10] the procedure for measuring potentials on a rotating disc cathode. The results of our measurements of the current yield of hydrogen and the cathode potentials in pure acid solutions of zinc sulfate and in the presence of sodium, magnesium, and calcium ions, and also analogous measurements from previous work in our laboratory [1, 9] are shown in Figs. 1 and 2. The current yields

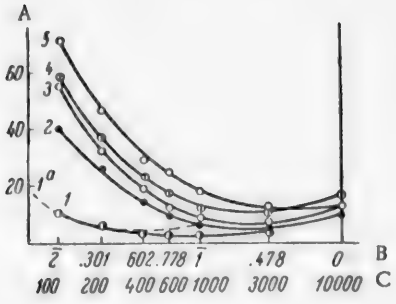

Fig. 1. Current yield of hydrogen during the electrolysis of sulfate solutions containing 60 g/liter of Zn and 100 g/liter of H_2SO_4 for pure solutions and for solutions with sodium, magnesium, and calcium ions added to the electrolyte in relation to current density at 30°. A) Current yield of hydrogen (in %); B) logarithm of current density (in a/cm^2); C) current density (in a/cm^2). 1) Pure solution and solution with added Na^+ (50 g/liter), Mg^{++} (25 g/liter), and Ca^{++} (saturated) —data from present work; 1[a]) pure solution—Pecherskaya's data; 2-5) Turomshina's data: 2) pure solution; 3) Ca^{++} (saturated); 4) Mg^{++} (25 g/liter); 5) Na^+ (50 g/liter).

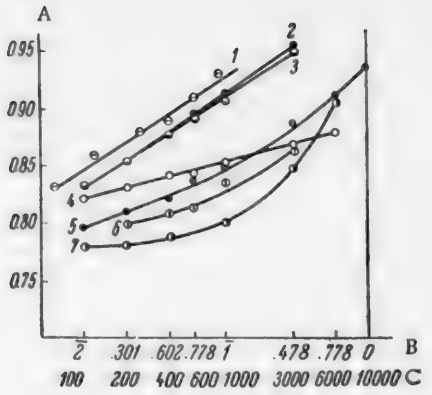

Fig. 2. Cathode potentials in the electrolysis of sulfate solutions containing 60 g/liter of Zn and 100 g/liter of H_2SO_4 for pure solutions and with sodium, magnesium, and calcium ions added to the electrolyte in relation to current density at 30°. A) Cathode potential (in v); B) logarithm of current density (in a/cm^2); C) current density (in a/cm^2). 1) Pure solution—Pecherskaya's data 2-3) present work: 2) Mg^{++} (25 g/liter), Na^+ (50 g/liter); 3) pure solution; 4-7) Turomshina's data: 4) pure solution; 5) Ca^{++} (saturated);6) Mg^{++} (25 g/liter); 7) Na^+ (50 g/liter).

of hydrogen which we measured (Fig. 1, curve 1) in pure solutions agreed with the data of Pecherskaya (broken line) and were considerably less than the yields determined by Turomshina (Fig. 1, curve 2); evidently, in the latter work, [1] despite recrystallization of the salt, the purity of the solution was insufficient for absolute comparisons. According to our observations, the current yield of hydrogen hardly changed when pure sodium, magnesium, and calcium salts were added to the electrolyte. In any case, the small fall in the current yield of zinc and the very small rise in the cathode potential may have been connected with certain diffusion phenomena (accumulation of foreign ions in the cathode boundary layer [9]), and not with a change in the mechanism of the electrode process (the formation and decomposition of intermetallic compounds).

Special 24-hour experiments on the electrolysis of pure acid solutions of zinc sulfate with added sodium (50 g/liter), magnesium (25 g/liter), and calcium (saturated solution) ions at a current density of 150-450 a/m^2 showed high and practically identical current yields of zinc, both for pure solutions and for solutions with additives. The cathode potentials we measured in pure solutions and in solutions with added calcium, magnesium, and sodium ions (Fig. 2, curves 2 and 3) were very close to the data of Pecherskaya and considerably more negative than the potentials determined by Turomshina (Fig. 2, curves 4-7). On the basis of the present work we consider that intermetallic compounds of zinc and sodium are not formed during the electrolysis of aqueous solutions containing sodium and zinc ions. There is the report in the literature [3] that alloys of zinc and sodium are formed by the reduction of solid zinc iodide or cyanide with metallic sodium in liquid ammonia; this may be so, but alloys of zinc and sodium are not formed under normal electrolysis conditions. We conclude that alkali and alkali earth metal ions in zinc electrolytes do not affect the current yield of zinc through the formation of intermetallic compounds and if there is a small effect, it is only due to the fact that the ions accumulate in the cathode boundary layer and hinder the approach of zinc ions to the cathode [9].

In conclusion we thank Prof. V. V. Stender for comments on the work.

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ELECTROLYSIS OF LITHIUM CHLORIDE SOLUTION WITH A MERCURY CATHODE

L. A. Alekseeva, G. I. Volkov, and É. I. Kus'kina

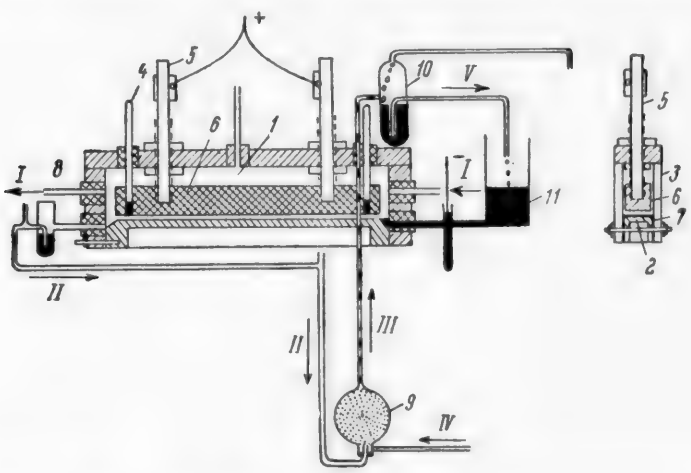
The well-known work of Sklyarenko and Sakharov [1] was devoted to a study of the electrolysis of lithium chloride solutions in an electrolyzer with a mercury cathode. In this work a special study was made of the effect of the lithium concentration in the amalgam on the current yield in electrolysis, and it was found that the current yield fell linearly with an increase in amalgam concentration.

The amalgam concentration was changed in the usual way by changing the rate of flow of mercury through the electrolyzer. The authors overlooked the fact that a change in the rate of mercury flow changed the nature of the motion of the stream through the electrolyzer and the time that the amalgam surface was in the electrolyzer. These factors themselves could have a stronger effect than the change in amalgam concentration.

A slower flow of the amalgam cathode leads to various impurities, which are of importance in the electrolysis process, remaining on the amalgam surface for a longer period. In addition, with a change in mercury flow rate, there is a change in the mixing of the cathode, since the Reynolds number changes, and, consequently, the conditions of withdrawal of the alkali metal into the layer are changed. We carried out some experiments which may be of interest.

EXPERIMENTAL

The experiments were carried out with a 35% solution of technical lithium chloride. The electrolysis was at a current density of about 2500 a/m^2 at 50-60°. The current consumption was determined by a copper coulometer



Plan of apparatus. 1) Electrolyzer; 2) copper trough; 3) glass plates; 4) thermometers; 5) anode rods; 6) graphite anode; 7) rubber gaskets; 8) shut-off device; 9) decomposer; 10) separator; 11) receiver bottle. I) Salt solution; II) amalgam; III) NaOH, Hg, H_2; IV) water; V) mercury.

and the cathode current yield by titration of the solution of lithium hydroxide obtained by decomposition of the amalgam. The hydrogen content of the chlorine was determined with an Orsat apparatus.

The plan of the apparatus is shown in the figure.

The electrolyzer was made of an inverted copper trough 2, to whose sides were cemented glass plates 3, forming walls. The ends of the electrolyzer were made of ebonite. The electrolyzer was covered with an ebonite lid, through which passed thermometers 4 and graphite anode rods 5, carrying current to the graphite anode 6. The cathode was 10 mm wide and 200 mm in length. The electrolyzer was sealed with rubber gaskets 7. The current to the cathode was carried by the stream of mercury entering the electrolyzer. Amalgam emerging from the electrolyzer passed through the shut-off device 8 and entered the decomposer 9, 25 ml in volume and filled with graphite pieces, 2-3 mm in size. Water was fed into the decomposer from the bottom. The hydrogen, liberated on decomposition of the amalgam, raised the mercury and alkali solution into the separator 10, whence the mercury returned by gravity into the electrolyzer through the receiver bottle 11. The flow of mercury from the seal 10 to the bottle 11 could be measured by collecting the mercury in a measuring cylinder.

At first an experiment was carried out at a flow rate which corresponded to the formation of an amalgam with a concentration of 0.002% at 100% current yield. The hydrogen content of the chlorine in this experiment was 22-25% and the current yield over 1 hour was 37%. During this experiment it was noticed that from approximately $^1/_3$ of the way from the beginning of the electrolyzer the cathode surface was covered with a grey coating and hydrogen bubbles. This film could be displaced to the end of the electrolyzer as the mercury flow rate increased and completely disappeared from the electrolyzer at an input rate of 150-200 ml/min of mercury, which corresponds to an amalgam concentration at the electrolyzer outlet of 0.0007% at 100% current yield.

At this mercury flow rate we were able to obtain a hydrogen content in the chlorine of about 3% and a current yield of 91.5% at 50-60°. To determine whether the process was improved by a reduction in the lithium concentration of the amalgam, we carried out the following experiment. By decreasing the water input into the amalgam decomposer, we tried to get incomplete decomposition of the amalgam and gradually increased its concentration without decreasing the mercury flow rate.

Data on electrolysis of a lithium chloride solution with an increasing amalgam concentration are given below.

Time from beginning of experiment (in min)	5	10	20	30	40	50	60	70	80
Mercury flow rate (in ml/min)	180	210	210	220	200	150	150	180	180
Temperature (in °C)									
at inlet . .	63	63	62	63	62	62	62	62	63
at outlet .	53	53	53	54	52	52	52	52	52
Amalgam concentration (%)		0.0007	—	0.0016	0.0027	0.0030	0.0038	0.0035	0.0044
Chlorine analysis									
Cl_2	92.7	92.7	92.9	93.8	93.7	94.6	95.1	94.1	95.4
H_2		4.0	6.7	4.0	3.3	3.3	3.3	3.3	3.3

Unfortunately we were unable to raise the amalgam concentration even higher, but the experiment presented shows that role of the rate of movement of the amalgam cathode is even more important than the rôle of the amalgam concentration.

SUMMARY

In experiments on the electrolysis of a solution of technical lithium chloride at different linear velocities of the mercury cathode it was shown that a change in the rate of movement of the cathode can have a greater effect on the hydrogen liberation on the amalgam cathode than a change in the amalgam concentration.

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TEMPERATURE AND AMALGAM CONCENTRATION DEPENDENCE OF THE RATE OF AMALGAM DECOMPOSITION IN A SHORT-CIRCUITED CELL

G. I. Volkov and R. Ya. Emdina

To calculate the work of amalgam decomposers, it is necessary to know the relation between the rate of amalgam decomposition and its concentration. Industrial experience shows that this relation is important. When an amalgam decomposer no longer decomposes the amalgam completely, the residual undecomposed amalgam is again returned to the decomposer and if an increase in the amalgam concentration does not increase the decomposition rate, then the accumulation of alkali metal in the amalgam would very rapidly lead to crystallization of the amalgam. In actual fact the amalgam concentration grows very slowly and a bath operates with incomplete decomposition of the amalgam for very long periods.

The relation between the decomposition rate of an amalgam and its concentration is evidently determined by the change in emf of the amalgam cell due to the concentration of alkali metal in the amalgam.

The method measuring the rate of amalgam decomposition, developed previously by Volkov and Klitsa [1], makes it possible to determine the relation between the decomposition rate and the amalgam concentration without changing the actual concentration. The decomposition rate is determined from the strength of the current passing through an amalgam cell when the potential difference between its poles equals zero. If the current strength is measured at several values of the potential difference between the poles of the amalgam cell, then by using the relation between the potential of the amalgam and its concentration, it is possible to convert these potential differences to amalgam concentrations and derive a relation between the amalgam decomposition rate and its concentration.

The experiments were carried out with an amalgam cell whose design is shown in Fig. 1.

Into a 300-ml glass beaker was poured 100 ml of sodium amalgam of known concentration and 50 ml of sodium hydroxide solution. The electrode was a graphite rod, 10 mm in diameter and 120 mm high, with a conical end of the following dimensions: the cone height was 1 mm and the diameter of the upper base was 8 mm. The separation between the graphite electrode and the amalgam was 3 mm. The graphite rod was covered with a perchlorovinyl varnish, with the exception of the working parts, and then the whole length down to the cone was insulated with rubber tubing.

The graphite electrode was treated before each experiment to avoid a sharp fall in the activity of the graphite, which occurs in the first hours of operation of the decomposer. For this purpose the poles of the cell were connected through a milliammeter until a constant current strength was reached (after 1 hour).

An electric plate was used for heating the cell. The cell was placed in a glass beaker, which served as a water bath. The experiment was carried out at temperatures of 20-80° with measurements at 10° intervals. The current strength in the circuit of the amalgam cell was measured with a milliammeter and the potential difference across the poles of the cell was determined with a millivoltmeter with the aid of a rheostat.

The measurement results are presented in Fig. 2.

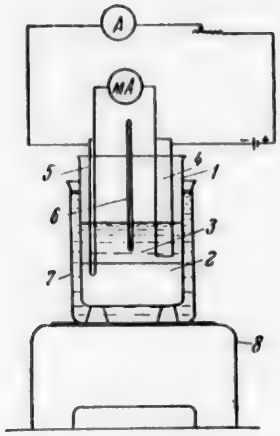

Fig. 1. Plan of apparatus for measuring the rate of amalgam decomposition in a short-circuited cell. 1) Glass beaker; 2) sodium amalgam; 3) sodium hydroxide; 4, 5) electrodes; 6) thermometer; 7) beaker (water bath); 8) electric plate.

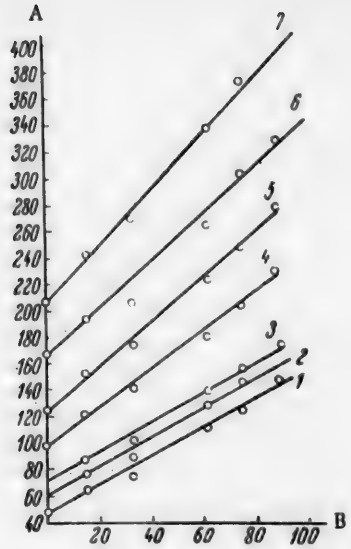

Fig. 2. Relation between current strength in amalgam cell and the potential difference of its poles. A) Current strength (in ma); B) potential difference (in mv). Temperature (in °C): 1) 20, 2) 30, 3) 40, 4) 50, 5) 60, 6) 70, 7) 80.

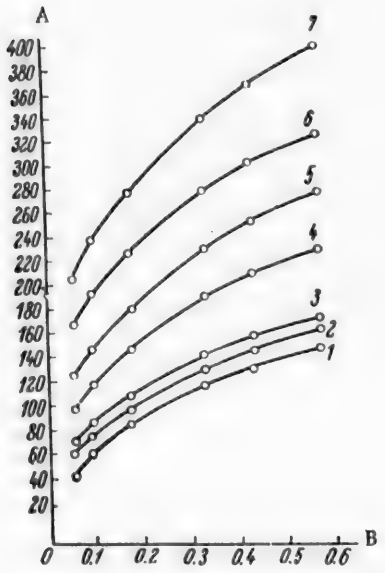

Fig. 3 Calculated relation between current strength in amalgam cell and amalgam concentration. A) Current strength (in ma); B) amalgam concentration (in %). Temperature (in °C): 1) 20, 2) 30, 3) 40, 4) 50, 5) 60, 6) 70, 7) 80.

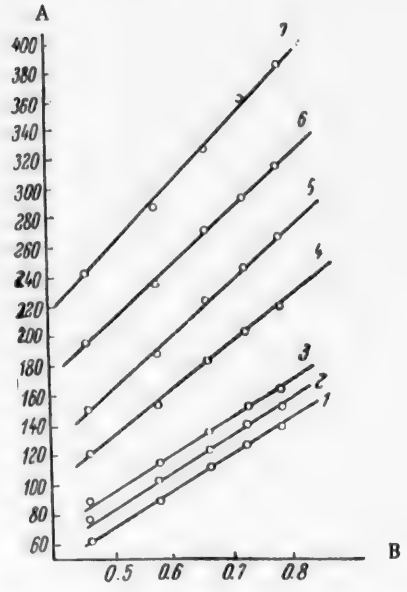

Fig. 4. Relation between current strength in amalgam cell and amalgam concentration. A) Current strength (in ma); B) value of $\sqrt[3]{c}$. Temperature (in °C): 1) 20, 2) 30, 3) 40, 4) 50, 5) 60, 6) 70, 7) 80.

The amalgam concentration at the beginning of the experiment was 0.060% of Na and at the end, 0.051%, i.e., an average of 0.055%.

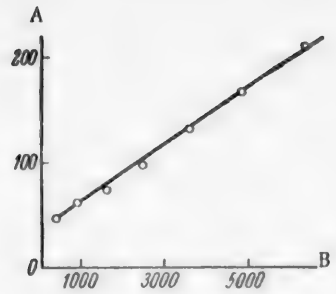

Fig. 5. Relation between current strength in amalgam cell and temperature. A) Current strength (in ma); B) value of t^2.

The potential differences were converted into amalgam concentrationsby means of the data of Trümpler and Schuler [2]. The relation between the rate of amalgam decomposition and its concentration obtained is given in Fig. 3. This relation may be expressed by the following equation with sufficient accuracy for technical calculations:

$$I = k\sqrt[3]{c} + 0{,}13k, \qquad (1)$$

and confirmation of this is given in Fig. 4, where the cube root of the amalgam concentration c is plotted along the abscissa and the value of the value current strength I (in ma), along the ordinate. The value of the constant k for 80° equals 415. It is understood that this value of k refers only to the given cell, but knowing the current strength of any other cell at a given amalgam concentration it is possible to calculate the value of the constant from equation (1).

The temperature dependence of the current strength of the amalgam cell may be expressed by the following equation

$$I = a + 0{,}00075\ at^2. \qquad (2)$$

For the given cell and an amalgam concentration of 0.06% the value of a = 36 when the current strength is expressed in milliamperes. In confirmation of the given temperature dependence of the rate of amalgam decomposition, we give Fig. 5, where the latter value is given in relation to the square of the temperature.

The equations obtained make it possible to calculate the dimensions of amalgam decomposers with a change in their operating conditions.

The nature of the relation between the current strength in an amalgam cell and the value of the applied external emf (Fig. 3) makes it possible to decide whether it is advantageous to convert amalgam decomposers into electrolytic baths or whether it is sufficient to apply a voltage of 0.1 v to double the amalgam decomposition rate, i.e., reduce the working dimensions of the amalgam decomposer by a factor of two. For baths operating at high current densities, the consumption of a small amount of electrical energy may be quite justified by the economy in mercury filling the decomposer, the economy in mercury losses due to the decrease in the size of the decomposer, and the elimination of forced shutdowns of the baths, arising as a result of decomposer breakdowns.

SUMMARY

In a model cell of sodium amalgam, alkali solution, and graphite we measured the relation between the current strength and the extemally applied voltage at various temperatures. The measurements were used to calculate the relation between the rate of amalgam decomposition and its concentration and temperature and suitable equations are given for these relations for technical calculations.

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DETERMINATION OF THE TRILON B CONTENT OF ACID TINPLATING ELECTROLYTES

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In recent years there has been wide application of new chemical reagents—complexones [1, 3], which give stable and readily soluble compounds with a whole series of cations. Complexones have found wide application in analytical chemistry and at the present they are beginning to find industrial application, in particular, in chemical machine construction. Trilon B (Complexone III) is introduced into the tinplating electrolyte to prevent hydrolysis of the tin and its precipitation, and this considerably increases the stability of the electrolyte. In the tinplating process it is necessary to maintain a definite Trilon B concentration in the solution, and consequently it is necessary to check the content periodically.

In developing a method for determining Trilon B in an acid tinplating electrolyte we used two volumetric methods.

The first method was based on the titration of Trilon B with a standard solution of magnesium chloride with the indicator Chromagen Special Black E-00 [4]; in the second method a solution of calcium chloride was used in the presence of ammonium oxalate as indicator [5]. In both cases, in the analysis of Trilon B in Tinplating electrolyte the tin present interfered and this was removed by precipitation with hydrogen sulfide in an acid medium.

For developing the methods we prepared synthetic mixtures, corresponding to the composition of electrolytes used for tinplating.

Mixture I (in g/liter)		Mixture II (in g/liter)	
$SnCl_2$	56.0	$SnSO_4$	54.0
HCl	8.0	H_2SO_4	70.0
Phenol	4.7	Phenolsulfonic acid	50.0
Dextrin	1.0		
Boric acid	10.0		
NaF	38.0		

Into these mixtures were introduced accurately measured amounts of Trilon B solution. The Trilon B content of the electrolytes was then determined by the two methods mentioned above—titration with magnesium chloride solution and with calcium chloride solution. The data obtained are given in the table.

As can be seen from the data presented, the accuracy of the determination of Trilon B in acid tin solutions by both methods is quite satisfactory. The determination error does not exceed 3.2%.

On the basis of the investigations, two methods were developed for determining Trilon B in acid tinplating electrolytes.

Before determination of the Trilon B, in both cases the tin was precipitated by passing H_2S through the acid solution analyzed. The stannous sulfide precipitate was removed by filtration, washed with water, saturated with H_2S, and discarded. The filtrate was boiled until all the H_2S had been removed.

Results of Determining the Trilon B Content of Acid Tinplating Electrolytes

Trilon B (in mg)		Difference		Trilon B (in mg)		Difference	
taken	found by 1st method	in mg	in %	found by 1st method	found by 2nd method	in mg	in %
22.57	22.40	−0.17	0.75	22.57	21.98	−0.59	2.61
22.57	22.40	−0.17	0.75	22.57	22.24	−0.33	1.46
22.57	22.74	+0.17	0.75	22.57	22.24	−0.33	1.46
22.57	22.81	+0.24	1.06	22.57	22.69	+0.12	0.53
22.57	22.20	−0.37	1.63	45.14	43.68	−1.46	3.23
45.14	44.90	−0.24	0.53	45.14	44.69	−0.45	1.0
45.14	44.00	−1.14	2.52	45.14	44.21	−0.99	2.06
45.14	44.90	−0.24	0.53	45.14	45.49	+0.35	0.77
45.14	44.40	−0.74	1.63	45.14	45.43	+0.29	0.64
45.14	45.36	+0.22	0.48	45.14	45.31	+0.17	0.37
45.14	45.41	+0.27	0.60	45.14	43.68	−1.46	3.23

For determination of the Trilon B by the first method, the filtrate was neutralized with ammonia to methyl red, 5 ml of buffer solution (5.4 g of NH_4Cl + 35 ml of NH_4OH in 100 ml of H_2O) added followed by a small amount of the indicator Chromagen Special Black ET-00 to an appreciable blue color, and the solution titrated with 0.02 N $MgCl_2$ solution until the color of the solution changed to wine red.

For determination by the second method, the filtrate was neutralized with ammonia and titrated with 0.1 N $CaCl_2$ solution in the presence of ammonium oxalate until an appreciable turbidity was produced. The titration was carried out with illumination of the solution from the side.

SUMMARY

1. Two methods were developed for determining Trilon B in acid tinplating electrolytes by titration with $MgCl_2$ and $CaCl_2$ solutions.

2. It was established that both methods give quite satisfactory results.

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CONDENSATION OF HEXAMETHYLDISILOXANE IN SILENT DISCHARGES

D. N. Andreev

Under the action of silent electrical discharges, many compounds are capable of condensing to form various condensation products. As we showed previously [1, 2], this method may also be used for condensation of organosilicon compounds. Thus, for example, starting from methylchlorosilanes [CH_3SiCl_3 and $(CH_3)_2SiCl_2$], we obtained compounds containing in the main chain alternate silicon and carbon atoms: $\equiv Si-CH_2-Si\equiv$, $\equiv Si-CH_2-CH_2-Si\equiv$, $\equiv Si-CH_2-\underset{|}{Si}-CH_2-Si\equiv$, etc.

Continuing the investigations on the condensation of organosilicon compounds in silent discharges, we condensed hexamethyldisiloxane [$(CH_3)_3Si-O-Si(CH_3)_3$]. It might have been expected that in this case we would obtain compounds containing alternate Si, C, and O atoms in the main chain.

The condensation experiments were carried out in a glass reactor by the method described previously [2] with the only difference that instead of hydrogen, a nitrogen atmosphere was used. It was established that even at 8 kv (at which the discharge began) traces of acetylene appeared in the emergent gases, indicating partial rupture of $Si-CH_3$ bonds and the formation of $\cdot CH_3$ radicals.

The appearance of acetylene in the gas was the result of further conversions of the methyl radicals. With an increase in the voltage of the current, the acetylene content (determined qualitatively by Ilos reagent) increased. However, we were unable to establish the presence of acetylene or olefins and saturated hydrocarbons in the gas by a volumetric method. In addition to nitrogen, the gases contained only 1.2-1.3 vol. % of H_2. This indicated that under our experimental conditions, the main process occurring under the action of electrical discharges was condensation and not cracking.

In order to determine how a change in the discharge parameters affected the yield of condensation products, we carried out a series of experiments at different voltages.

The results of the experiment are given below.

Experiment No.	4	5	6	8
Voltage in secondary circuit (in kv)	15.5	21.5	23.0	23.0
Current in secondary circuit (in ma)	1.65	2.45	2.65	2.65
Discharge power (in va)	25.7	52.7	60.9	60.9
Experiment duration (in hr)	31.	32.2	32.2	63.8
Yield of condensation products, calculated on starting siloxane (in %)	4.6	8.7	15.8	26
Yield of condensation products, calculated on siloxane reacting (in %)	33	45	53	70

From the data presented above it follows that by the prolonged action of such a discharge at 23 kv it is possible to achieve a yield of condensation products of 26%, calculated on the starting siloxane, and 70%, calculated on the siloxane reacting.

To accumulate condensate, we carried out a series of experiments at 23 kv. As a result of an investigation of the condensation products, it was established that about 75% of the condensate was compounds containing 3-4 Si atoms in the molecule, formed as a result of the condensation of two molecules of hexamethyldisiloxane or, more accurately, two radicals formed from molecules of this siloxane. The remaining 25% of the condensate consisted of higher condensation products, containing 5 or more Si atoms in the molecules. The high-boiling fractions of the condensate were decolorized with $KMnO_4$ solution, indicating the presence of unsaturated compounds in them.

Investigation of separate fractions of condensate made it possible to establish that they contained the following compounds: 1) octamethyltrisiloxane, 2) (trimethylsiloxymethyl) heptamethyltrisiloxane, which was apparently a mixture of two isomers, 3) a compound with the composition $C_{12}H_{34}O_3Si_4$ and 4) a compound with the composition $C_{13}H_{38}O_4Si_5$.

1. Octamethyltrisiloxane: b.p. 145-155°, d_4^{20} 0.8195, n_D^{20} 1.3864. Literature data [3]: b.p. 152°, d_{25}^{25} 0.8182, n_D^{25} 1.3822; [4]: b.p. 152.5°, d_4^{20} 0.8200, n_D^{20} 1.3849.

2. (Trimethylsiloxymethyl) heptamethyltrisiloxane: b.p. 190-195°, d_4^{20} 0.8496, n_D^{20} 1.3968.

Found %: Si 35.32; C 40.40, H 10.12; MR_D 91.98

$C_{11}H_{32}O_3Si_4$. Calculated %: Si 34.59, C 40.68, H 9.93; MR_D 91.84

This compound was probably a mixture of two isomers, differing in the position of the trimethylsiloxy group.

3. Compound with the composition $C_{12}H_{34}O_3Si_4$: b.p. 102-107° (20 mm), d_4^{20} 0.8498, n_D^{20} 1.4028.

Found %: Si 34.04, C 41.89, H 10.23; MR_D 97.28.

$C_{13}H_{34}O_3Si_4$. Calculated %: Si 33.17, C 42.55, H 10.12; MR_D 97.48.

The molecular refraction was calculated for bis (trimethylsiloxymethyl) tetramethyldisiloxane.

4. Compound with the composition $C_{13}H_{38}O_4Si_5$: b.p. 145-155° (20 mm), n_D^{20} 1.4035, d_4^{20} 0.8832.

Found %: Si 34.65, C 39.55, H 9.69; MR_D 110.37

$C_{13}H_{38}O_4Si_5$. Calculated %: Si 35.20, C 39.13, H 9.60; MR_D 110.48.

The molecular refraction was calculated for 2,2,4,4,6,6,9,9,11,11, -decamethyl-2,4,6,9,11-pentasila-3,5, 8,10-tetraoxadodecane.

The compound with the composition $C_{12}H_{34}O_3Si_4$ was assumed to be bis(trimethylsiloxymethyl) tetramethyldisiloxane, for which two isomers are possible. The second compound with the composition $C_{13}H_{38}O_4Si_5$ corresponded in composition and molecular refraction to 2,2,4,4,6,6,9,9,11,11-decamethyl-2,4,6,9,11-pentasila-3, 5,8,10-tetraoxadodecane.

The work demonstrated the possibility of condensing hexamethyldisiloxane in silent discharges to form polymeric compounds of low molecular weight, mainly of linear structure and containing alternate silicon, carbon, and oxygen atoms in the main chain.

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PLASTICS BASED ON PHENOL ALCOHOLS AND GYPSUM (GYPSORESITES)

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Instead of bakelite resins, for the production of various forms of phenol-aldehyde plastics it is possible to use aqueous solutions of the initial products of the reaction of phenol with formaldehyde (phenol alcohols) [1], which change into bakelite resins on heating and then into resites. Phenol alcohols are obtained in the presence of bases at moderate temperatures. Being miscible with water in all proportions, they do not require the use of organic solvents and may be used successfully for the impregnation of fibrous and other materials. By the method developed by the authors of the present article, phenol alcohols were used by Zhuravlev and Vol'fson to impregnate slabs of reinforced autoclave gypsum, which they proposed as a new type of electrical insulating material instead of marble for the manufacture of low-voltage distributing boards [2]. The boards successfully withstood test operation for a number of years in an atmosphere of high humidity.

In our experiments gypsum slabs were impregnated with an undiluted solution, containing about 50% of phenol alcohols, 15% of phenols, and 35% of water. It is also possible to use solutions containing larger amounts of phenol alcohols and smaller amounts of phenol. The thermal treatment of the impregnated slabs to remove the water, resinify the phenol alcohols, and harden the resins consisted of gradually raising the temperature from 60 to 110° over approximately 20 hours. The shortcoming of the method is the need for removing from the impregnated slabs the considerable amount of water contained in the solution of phenol alcohols.

The problem of preparing electrically insulating plastics, based on phenol alcohols and gypsum(gypsoresites), could also be solved by another method, namely, by binding the gypsum not with water, but directly with aqueous solutions of phenol alcohols, taken in such an amount that all the water contained in them was bound by the gypsum, converting it from the hemihydrate to the dihydrate. Since 100 parts of gypsum hemihydrate require 18 parts of water for this conversion and the aqueous phenol alcohols contain about 35% of water, simple calculation shows that if 100 parts of gypsum hemihydrate are mixed with 50 parts of aqueous phenol alcohols, then after setting, the mixture must consist of gypsum dihydrate and anhydrous phenol alcohols. As our experiments showed, mixing the components in this proportion yielded a plastic, readily molded mass which set rapidly. Gradually heating the mass under the conditions indicated above yielded a material which was more homogeneous and less porous than that prepared by impregnation. Plastics obtained by this and by the other method contained 18-19% of resin in stage "C".

The table gives the results of testing plastics (gypsoresites) based on autoclave gypsum, reinforced with wool combings, and phenol alcohols.

The introduction of the phenol-aldehyde resin into the gypsum composition led to a considerable increase in the tensile strength of the material (by a factor of almost two), and both the setting method and the impregnating method gave samples with approximately the same indices (about 60 kg/cm^2).

The new method proposed for preparing gypsoresites, based on binding gypsum with phenol alcohols and subsequent thermal treatment of the set mass, makes it possible to improve the quality of the material as regards homogeneity and resistance to atmospheric moisture.

Comparative Results of Electrical Testing of Gypsoresites, Obtained by the Binding Method and by the Impregnating Method, and of Gypsum, Not Treated with Phenol Alcohols

Material	Property	Results of testing samples			
		in original state	tested after 24 hr in an atmosphere with 100% relative humidity		
			immediately	after 20 min	after 24 hrs
Reinforced autoclave gypsum (not treated with phenol alcohols)	Specific surface resistance (in Ω)	$4.0 \cdot 10^9$	$1.6 \cdot 10^6$	$2.7 \cdot 10^6$	$1.0 \cdot 10^9$
	Specific volume resistance (in Ω · cm)	$4.0 \cdot 10^9$	$1.0 \cdot 10^6$	–	–
Gypsoresite, obtained by binding method	Specific surface resistance (in Ω)	$4.0 \cdot 10^{10}$	$2.7 \cdot 10^9$	–	$3.0 \cdot 10^{10}$
	Specific volume resistance (in Ω · cm)	Above 10^{10}	$4.0 \cdot 10^9$	$1.0 \cdot 10^{10}$	Above 10^{10}
Gypsoresite, obtained by impregnation method	Specific surface resistance (in Ω)	$1.6 \cdot 10^{10}$	$1.6 \cdot 10^7$	$6.0 \cdot 10^7$	$1.0 \cdot 10^{10}$
	Specific volume resistance (in Ω · cm)	$1.0 \cdot 10^{10}$	$1.5 \cdot 10^7$	–	$5.0 \cdot 10^9$

The marble usually used for distributing boards has a beautiful external appearance and is of comparatively low cost, but has a number of drawbacks (friability, inhomogeneity, considerable expenditure of labor in processing, lack of acid-resistance, a considerable fall in the electrical resistance properties under the actions of moisture and a slow recovery of these properties, etc.).

The simplicity of the production of gypsoresites, the low cost, which is no higher than that of marble, and the good mechanical and electrical properties make it possible to predict that they may be used instead of marble for the manufacture of low-voltage distributing boards. Plastics based on phenol alcohols and gypsum are homogeneous, mechanically strong, and not friable. They have a good chemical resistance, especially towards acids. The electrical insulating properties of the materials described are reduced comparatively little by the action of moisture and are rapidly recovered after the materials are removed from the moist atmosphere. The manufacture of the plastics is simple and does not require much work.

SUMMARY

We propose the use of aqueous solutions of phenol alcohols for binding gypsum and for impregnating gypsum slabs with subsequent thermal treatment of the materials under conditions for resinifying the phenol alcohols and hardening the bakelite resins. The plastics obtained are strong, heat-, water-, and chemically resistant materials with good electrical insulating properties. The best dielectrical properties are possessed by resins obtained by the binding method.

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CHEMICAL NATURE OF PETROLEUM ASPHALTENES

S. R. Sergienko and S. D. Pustil'nikova

Asphaltenes are chemically the most complex components of crude petroleums, which, as a rule, are found in heavy petroleums and natural asphalts in the form of colloidal particles. The dimensions of such particles (micelles), according to the data of various investigators, vary over quite a wide range: particle diameters from 30 to 100 A and molecular weight from 5000 to 200,000.

In our investigations [1] it was shown that when the molecular weight of asphaltenes is determined cryoscopically under conditions which exclude association of the molecules (in naphthalene at a temperature above 80°), the molecular weight varies about 2000.

Elementary analysis of asphaltenes shows that heteroatoms such as sulfur, oxygen, nitrogen, and metals (V, Ni, Fe, Co, Ti, etc.) begin to play an important part in their molecules.

However, despite the considerable specific gravity of the heteroatoms, the carbon skeleton determines the main structural characteristics of these very large petroleum molecules.

Therefore, it seemed important to achieve the conversion from asphaltenes to hydrocarbons without rupture of the C–C bonds in their carbon skeleton. Such a conversion should be an important step towards elucidating the structure of asphaltene molecules. Selective catalytic hydrogenation at comparatively low temperatures seemed to us to be the most suitable method for solving this problem.

In a previous investigation [2] it was shown on the example of high-molecular compounds of petroleum, containing condensed aromatic nuclei in the molecule, that the product could be desulfurized almost completely in the presence of Raney nickel at 150° with an operating hydrogen pressure in the autoclave of 150 atm and a hydrogenation time of from 10 to 30 hours. At the same time there was also appreciable saturation of the aromatic rings with hydrogen, but hardly any cracking, i.e., rupture of a simple C–C bond was observed. Preliminary experiments on the hydrogenation of asphaltenes under the same conditions and over the same catalyst showed that in this case the hydrogenation proceeded in the same direction. The amount of catalyst and, to a lesser extent, the hydrogenation duration considerably affected the degree and depth of conversion of asphaltenes. The asphaltenes were hydrogenated in cyclohexane solution in a rotating autoclave for a total time of 50 hours. The catalyst taken at the beginning of the experiment was 150% of the charge of asphaltenes, and then after each 10-hour period a fresh portion of catalyst with the same weight was added. The temperature was 150° and the working hydrogen pressure 150 atm.

The residual asphaltenes were precipitated from the hydrogenation products, and the remaining reaction products were separated chromatographically on coarsely porous silica gel by the method described previously [3, 4].

Table 1 and also Figs. 1 and 2 give data characterizing the composition and properties of the products obtained by hydrogenation of asphaltenes from Romashkin (Devonian) petroleum. Under the selective hydrogen conditions described, it was possible to convert the asphaltenes by the general scheme: asphaltenes → resins → → hydrocarbons. With a hydrogenation time of 50 hours, 55% of the asphaltenes were hydrogenated and of them, 12% were converted to high-molecular hydrocarbons and 43% to resins. The group composition of the hydrocarbons obtained by selective catalytic hydrogenation of petroleum asphaltenes and also the properties and composition of separate groups of hydrocarbons are given in Table 2.

TABLE 1

Composition and Properties of Asphaltene Hydrogenation Products

Stage	Component of hydrogenation product	Composition (in %)	Molecular wt.	Elementary composition (in %)			
				C	H	S	O (by difference
I	Total hydrogenation product	100	—	86.05	8.28	3.50	2.07
	Asphaltenes	79	1700	83.76	8.14	3.65	4.45
	Resins	17	963	86.39	9.45	2.61	1.55
	Hydrocarbons	4	350	88.08	10.06	1.76	—
II	Total hydrogenation product	100	—	85.81	8.58	2.66	2.95
	Asphaltenes	65	1990	85.06	8.29	3.26	3.39
	Resins	28	1005	85.87	9.82	1.38	2.93
	Hydrocarbons	7	342	88.21	10.91	0.81	—
III	Total hydrogenation product	—	—	86.19	8.90	2.65	2.26
	Asphaltenes	56	2415	86.02	8.43	3.63	1.92
	Resins	35	1115	86.08	9.75	1.50	2.67
	Hydrocarbons	9	319	88.68	10.57	0.59	—
IV	Total hydrogenation product	100	—	85.96	8.74	2.94	2.36
	Asphaltenes	50	2775	84.36	8.15	3.61	3.88
	Resins	40	1125	86.45	9.75	1.00	2.80
	Hydrocarbons	10	299	88.70	10.60	0.68	—
V	Total hydrogenation product	100	—	85.75	8.36	3.20	2.69
	Asphaltenes	45	3250	84.51	8.11	3.72	3.66
	Resins	43	1070	85.50	10.26	0.85	3.39
	Hydrocarbons	12	302	88.00	11.46	0.54	—

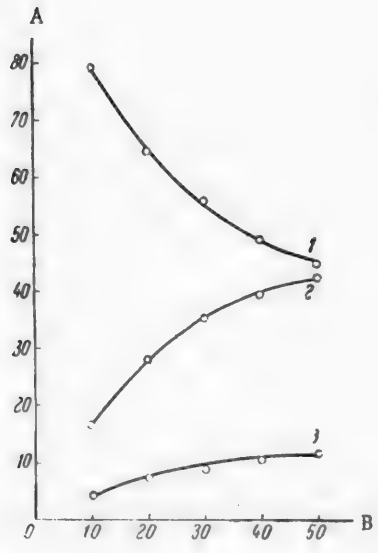

Fig. 1. Composition of hydrogenation products at various stages of hydrogenation A) Content (in %); B) time (in hr). 1) Asphaltenes; 2) resins; 3) hydrocarbons.

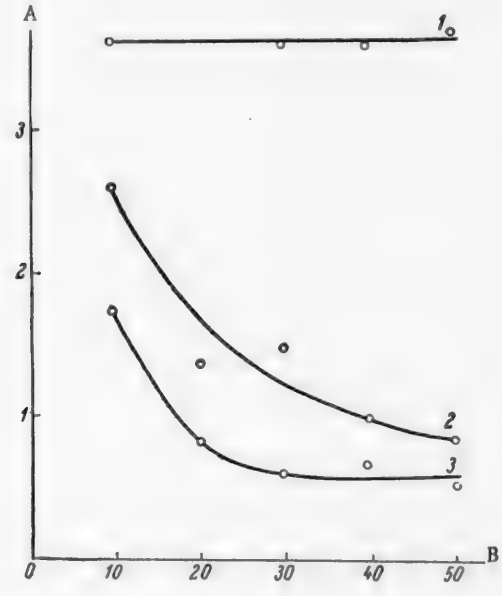

Fig. 2. Sulfur content of reaction products at various stages of hydrogenation. A) Sulfur content (in %); B) time (in hr). 1) Asphaltenes; 2) resins; 3) hydrocarbons.

TABLE 2

Composition and Properties of Hydrocarbons Obtained by Hydrogenation of Asphaltenes and Isolated from Romashkin Petroleum

Hydrocarbon group	Properties			Elementary composition (%)			Structural group composition					
							No. of rings			%		
	M	n_D^{20}	d_4^{20}	C	H	S	R_O	R_A	R_{cp}	C_a	C_{cp}	C_p
Paraffino-cycloparaffin (p. c.p.) Isolated from petroleum.	365	1.4709	0.8427	85.83	14.04	—	1.2	—	1.2	—	24	76
Paraffino-cycloparaffin (p. c.p.) Obtained by hydrogenation.	322	1.4755	0.8691	85.81	13.74	0.23	2.1	—	2.1	—	45	55
Monocycloaromatic. isolated from petroleum.	400	1.5113	0.9184	85.87	12.21	1.58	2.7	1.1	1.6	22	22	56
Monocycloaromatic. Obtained by hydrogenation.	338	1.5258	0.9445	87.37	11.80	0.56	2.9	1.2	1.8	28	29	43
Bicycloaromatic. Isolated from petroleum.	374	1.5700	0.9933	85.32	10.22	4.32	3.9	2.3	1.6	41	24	35
Bicycloaromatic. Obtained by hydrogenation.	440	1.5890	1.0268	89.52	10.07	0.89	5.3	3.0	2.3	43	29	28
Polycycloaromatic obtained by hydrogenation of asphaltenes.	428	1.6110	1.0431	89.14	9.48	2.18	5.4	3.6	1.7	52	22.0	26

Comparison of the composition and properties of high-molecular hydrocarbons, isolated from crude Romashkin petroleum, with those of hydrocarbons obtained by hydrogenation of asphaltenes (Table 2) shows that the latter have a higher degree of cyclization, which affects all their properties. The bicycloaromatic hydrocarbons have a particularly high degree of cyclization.

Among the hydrocarbons obtained by hydrogenation of asphaltenes, polycyclic aromatic hydrocarbons represented more than 40%, while this group of hydrocarbons could not be detected at all in the high-molecular hydrocarbons isolated directly from crude petroleum. These data indicate that both the over-all degree of cyclization and degree of condensation of the cyclic systems in the asphaltene molecules are considerably higher than in the high-molecular hydrocarbon part of petroleum. The high degree of condensation in the cyclic structures in asphaltene molecules and the predominance of aromatic chains in these condensed cyclic systems determine both the composition and the chemical and physical properties of asphaltenes.

The sharp fall in the molecular weight of resins and hydrocarbons obtained by mild, selective hydrogenation of asphaltenes indicates that the heteroatoms, primarily sulfur and oxygen atoms, are not only incorporated in cyclic structures (heterocycles), but also form bridges between separate polycyclic systems forming part of the asphaltene molecules. The data obtained in our investigation is a direct indication of the existence of a genetic link between petroleum asphaltenes, resins, and high-molecular hydrocarbons.

With respect to degree of cyclization and content of aromatic structural units in the molecule, the aromatic hydrocarbons obtained by hydrogenation of asphaltenes occupy an intermediate position between resins and high-molecular aromatic hydrocarbons isolated from the same crude petroleum.

Low-temperature catalytic hydrogenation makes it possible to convert asphaltenes to resins and high-molecular hydrocarbons similar in composition and properties to the components of crude petroleum. This result is of fundamental scientific importance in the understanding of the geochemical history of petroleum and for elucidating the chemical nature of asphaltenes.

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OXIDATION OF HYDROQUINONES TO QUINONES

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As is well-known, hydroquinones may be oxidized to quinones with many reagents. The reaction is most frequently carried out in a strongly acid medium; there are few convenient preparative methods of oxidation in weakly alkaline, neutral, or weakly acid media. The need for oxidation of hydroquinones in the absence of strong acids arose, in particular, because some quinones are extremely sensitive to acids [1]. Appreciable acidity of the medium in the preparation of quinones may also be inadmissible for a number of other reasons.

It might have been expected that a convenient reagent for oxidation of hydroquinones under conditions dispersing with a strongly acid medium would be hypobromite. There is no information in the literature on the use of hypobromite for oxidizing hydroquinones to quinones. We studied the action of sodium hypobromite on hydroquinone, chlorohydroquinone, and 2-methyl-1, 4-naphthohydroquinone. These substances were oxidized smoothly by hypobromite in the presence of a small amount of sulfuric acid to form the corresponding quinones in high yields. In the preparation of p-benzoquinone, the reaction was best carried out in a homogeneous medium. The oxidation of hydroquinone in an aqueous solution proceeded readily even at 80°, making it possible to use relatively small volumes of water. The oxidation was complete after a few minutes. In a special experiment we measured the pH value (20°) of the starting hypobromite solution and the reaction mixture after oxidation; the pH values equaled 10.3 and 2.8, respectively. In a blank experiment (without hydroquinone) the hypobromite solution after addition of sulfuric acid had a pH value of 9.2 (after 5 min at 80°, i.e., under the reaction conditions, the medium also remained alkaline). An increase in the excess hypobromite from 25 to 100% raised the final pH value to 3.2. It should be noted particularly that even a slight further decrease in the acidity at the beginning of the reaction led to tar formation. Therefore, in preparing a hypobromite solution with a higher pH value it was necessary to increase the amount of sulfuric acid. The use of excess acid did not have a negative effect on the reaction.

During the work we showed that the oxidation of hydroquinone with bichromate in the presence of sulfuric acid by known procedures [2] always gave p-benzoquinone containing quinhydrone, which gave the product a greenish tinge. We looked for conditions under which the oxidation of hydroquinone by bichromate would proceed completely and rapidly. It was found that this could be achieved by carrying out the reaction at a comparatively high temperature (65-70°). Sufficient water was used to dissolve the intermediate quinhydrone. The oxidation was complete in approximately 1 minute.

EXPERIMENTAL

Preparation of Quinones by Oxidation of Hydroquinones with Hypobromite

p-Benzoquinone. To a solution of 11 g of hydroquinone in 125 ml of water and 2.8 ml of 2 N H_2SO_4 solution at 80° was added a solution of sodium hypobromite (from 10.5 g of 95% NaOH and 20 g of bromine in 55 ml of water). The reaction mixture (its temperature remained at about 80°) was stirred until a light-yellow solution was formed (1-3 minutes) and then rapidly cooled to 0°. The precipitated p-benzoquinone was collected, washed with 20 ml of ice water, and dried over calcium chloride. We obtained 8.25 g (76.3%) of quinone with m.p. 110.5-111°. Ether extraction of the aqueous solution yielded a further 2.11 g of quinone. The total yield was 96%. After recrystallization from aqueous alcohol, the substance had m.p. 114-115°.

Chloro-p-benzoquinone. To a solution of 1.45 g of chlorohydroquinone in 5.6 ml of 0.1 N H_2SO_4 solution was added a solution of hypobromite (from 1.05 g of NaOH and 2 g of bromine in 5 ml of water). The reaction mass heated up spontaneously (~ 50°); a dark oil separated and when stirred for 5 min it turned yellow and then crystallized. The chloro-p-benzoquinone was collected, washed with cold water, and dried over calcium chloride. The yield of material with m.p. 52.5-53.5° was 1.27 g (89%). After recrystallization from ligroin, the substance had m.p. 55-56°.

2-Methyl-1,4-naphthoquinone. To a sample of 0.87 g of 2-methyl-1,4-naphthohydroquinone in a mixture of 8 ml of alcohol, 3 ml of water, and 2.8 ml of 0.1 N H_2SO_4 solution at 20° was added a hypobromite solution (0.53 g of NaOH, 1 g of bromine, and 3 ml of water). The mixture was stirred for 5 minutes and cooled with ice and then the yellow precipitate of 2-methyl-1,4-naphthoquinone collected, washed with water, and dried. We obtained 0.8 g (93%) of substance with m.p. 103.5-104°. After recrystallization from alcohol, the substance had m.p. 104-104.5°. According to literature data [3] the m.p. is 105-106°.

Preparation of p-benzoquinone by oxidation of hydroquinone with bichromate. To a solution of 5.5 g of hydroquinone in 90 ml of water and 6.2 g of concentrated H_2SO_4 at 60° was added 7 g of $Na_2Cr_2O_7 \cdot 2H_2O$ in 10 ml of water (20°) in one portion with stirring. After approximately 1 minute (the temperature of the reaction mixture was ~65°), the mixture was rapidly cooled to 0° and the p-benzoquinone collected, washed with ice water (with two 10-ml portions), and dried. The yield of quinone with m.p. 111.5-112° was 4.4 g (81.4%).

SUMMARY

Hypobromite is proposed for oxidizing hydroquinones to quinones in the absence of a strongly acid medium. We obtained p-benzoquinone, chloro-p-benzoquinone, and 2-methyl-1,4-naphthoquinone in yields of 89-96%.

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SOME PHYSICAL PROPERTIES OF 2,4-TOLUYLENE DIISOCYANATE

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The literature contains hardly any data on the physical properties of isocyanates though these substances are finding increasing application in the production of synthetic high polymers.

Therefore, we considered it necessary to determine some physical properties of 2,4-toluylene diisocyanate, whose boiling (125° at 15 mm Hg) and melting (21.3°) points are known [1].

We investigated the following physical properties of 2, 4-toluylene diisocyanate: 1) density and viscosity • over the temperature range 20-90°; 2) saturated vapor pressure as a function of temperature over the range 100-155°; 3) refractive index of isocyanate solutions in chlorobenzene.

EXPERIMENTAL

Technical 2,4-toluylene diisocyanate was vacuum distilled twice on a distillation column with a packing height of 1.2 m. The packing consisted of standard Fenske rings. During the distillation we collected a narrow fraction boiling at 113° (7 mm Hg). The 2,4-toluylene diisocyanate content was determined analytically by the method described in BTU No. 13 Kh-05-58; it was found to equal 99.6 weight %. However, we should assume that the accuracy of this analytical method did not exceed ± 0.5 weight %. Spectral analysis showed the absence of impurities as the spectrum of a sample of 2,4-toluylene diisocyanate, specially prepared in the Scientific Research Institute of Organic Intermediates and Dyes, did not differ in any way from ours. No traces of the 2,6-isomer were detected. The spectral measurements on 2,4-toluylene diisocyanate were made • with cyclohexane and carbon disulfide on an IKS-12 spectrophotometer.

Density determination. The density of 2,4-toluylene diisocyanate was determined by means of a carefully graduated pycnometer with a narrow neck. The pycnometer had a volume of 4 cc. The possible error in the density measurements was $2 \cdot 10^{-4}$ g/cc. The temperature was kept constant (± 0.1°) with a TS-15 thermostat. The results of the density measurements are well described by the equation

$$d_t^4 = d_{25}^4 [1 - 8.31 \cdot 10^{-5} (t - 25)].$$

Viscosity determination. The viscosity of 2,4-toluylene diisocyanate was determined with an Ostwald viscometer with a capillary diameter of 1 mm. The temperature was kept constant (± 0.1°). From the average viscosity data we constructed a graph of $\lg \eta = f\left(\frac{1}{T}\right)$, which was a straight line.

From the slope of the line we calculated the viscous flow energy (E_{visc}), which was found to equal 3330 cal/mole.

The viscosity η for the whole temperature range was satisfactorily described by the equation

$$\eta = 0.0995\, e^{-\frac{3330}{RT}}.$$

•A co-worker in our laboratory, E. N. Boitsov, made the spectral measurements.

TABLE 1

t (in °C)	d_t^4 (in g/cc)	τ* (in sec)	η (in micropoises)	t (in °C)	d_t^4 (in g/cc)	τ* (in sec)	η (in micropoises)
25	1.2136	108	27.2	50	1.1880	68.5	16.9
30	1.2085	96	24.1	60	1.1779	59.5	14.5
35	1.2035	87.5	21.8	70	1.1679	52	12.6
40	1.1982	80	19.9	80	1.1580	46	11.0
45	1.1931	74	18.3	90	1.1480	42	10.0

* τ is the flow time.

TABLE 2

t (in °C)	P (in mm Hg)	t (in °C)	P (in mm Hg
100	12	130	39
105	16	135	46
110	19	140	54
115	24	145	63
120	28	150	73
125	33	155	85

The numerical values of the viscosity and density of 2,4-toluylene diisocyanate in relation to temperature are given in Table 1.

Determination of saturated vapor pressure. The saturated vapor pressure of 2,4-toluylene diisocyanate in relation to temperature was measured by the static method described in [2] on an apparatus kindly put at our disposal by a lecturer at Gor'kii State University, I. B. Rabinovich. The apparatus consisted of a tensimeter, a mercury manometer, a heating bath with a calcium chloride melt and a thermoregulator, and a vacuum apparatus with a system of taps.

The temperature was kept constant (± 0.1°). The accuracy of the vapor-pressure measurement was not less than 1 mm Hg.

The results of measuring the saturated vapor pressure of 2,4-toluylene diisocyanate are given in Table 2.

The results given above can be described satisfactorily by the equation

$$\lg P = -\frac{2342}{T} + 7.4006,$$

where P is the pressure (in mm Hg) and T the temperature (in °K).

From this equation we calculated the evaporation energy:

$$\lambda_{ev} - RT = 9700 \text{ cal/mole}.$$

Determination of refractive index. The refractive index n_D^{25} of solutions of 2,4-toluylene diisocyanate in chlorobenzene were determined on an Abbe refractometer at 25° with an accuracy of $1 \cdot 10^{-4}$ units.

The measurement results are given on the next page.

Isocyanate content (in weight %)	n_D^{25}
10.97	1.5385
90.34	1.5613
95.63	1.5640
97.67	1.5651
99.6	1.5658

DISCUSSION OF RESULTS

On the example of more than thirty liquids, Eyring and his co-workers [3] showed that the ratio of the evaporation energy to the viscous flow energy depends little on the nature of the liquid and equals 3 for unassociated liquids. Assuming that 2,4-toluylene diisocyanate is not associated, we obtained $3 \cdot E_{visc} = 3 \cdot 3330 = 9990$ cal/mole. This result agrees well with the value of the evaporation energy 9700 cal/mole, found by measuring the saturated vapor pressure, indicating the possibility of estimating the evaporation energy of other isocyanates from relatively simple viscosity measurements on the latter.

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PREPARATION OF 2-METHYLVALERALDEHYDE

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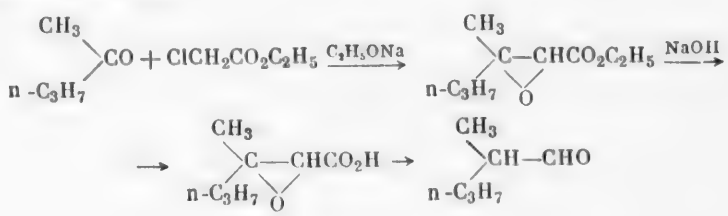
2-Methylvaleraldehyde is an intermediate in the synthesis of Meprotan, 2-methyl-2-n-propyl-1, 3-propanedioldicarbamate [1], which is a new drug for the treatment of nervous and psychic illnesses [2].

According to literature data, this aldehyde is obtained by reduction of α-methyl-β-ethylacrolein [3], by oxidation of 2-methylpentanol [4], and also by catalytic conversion of propanol [5] and allyl alcohol [6].

We developed a method of preparing 2- methylvaleraldehyde by decarboxylation of β-methyl-β-n-propylglycidic acid; the latter was prepared by hydrolysis of the ester, which was synthesized by condensation of methyl-n-propyl ketone with chloroacetic ester.



The preparation of 2-methylvaleraldehyde from methyl n-propyl ketone is of practical interest, as the starting materials are readily available. Methyl n-propyl ketone is found among the products of dry distillation of wood and forms 19% of the "white" acetone oil from which it is separated by distillation [7].

Methyl n-propyl ketone was condensed with ethyl chloroacetate in the presence of sodamide by Claisen [8] to give a 50% yield of product and in the presence of sodium ethylate by Martynov and Kastron [9]. The latter authors did not describe the experiment and reported only the yield, which was 57%, allowing for the unreacted ethyl chloroacetate.

Instead of the dry sodium ethylate usually used in the synthesis of glycidic esters, we used a freshly prepared paste of sodium ethylate to which was slowly added a mixture of the reagents with cooling. The temperature conditions, reaction duration, and other data were determined more accurately. The glycidic ester was separated without extraction with organic solvents as extraction of the aqueous layer raised the yield only very slightly. It was also established that, contrary to information in the literature [10], the use of more than a 25% excess of chloroacetic ester was not advantageous. The yield was 55% of theoretical, calculated on methyl n-propyl ketone.

Decarboxylation of β-methyl-β-n-propylglycidic acid and also preparation of the latter by hydrolysis of its ester are not described in the literature.

We carried out the hydrolysis in an aqueous sodium hydroxide solution with continuous distillation of the alcohol formed. The glycidic ester was gradually added to a previously heated alkali solution in order to avoid a vigorous reaction. When the mixture was acidified, the glycidic acid separated sufficiently completely in the form of an upper layer and was used for the preparation of 2-methylvaleraldehyde without purification.

β -Methyl-β -n-propylglycidic acid was decarboxylated by heating at a gradually increasing temperature, and as the 2-methylvaleraldehyde formed it was distilled in superheated steam. According to analysis the yield was 68% of theoretical, calculated on the ethyl glycidate.

EXPERIMENTAL

Ethyl β -methyl-β -n-propylglycidate. To sodium ethylate, prepared from 675 ml of absolute alcohol and 57.5 g (2.5 moles) of metallic sodium and cooled with stirring to -10°, was added a solution of 172 g (2 moles) of methyl n-propyl ketone in 306.4 g (2.5 moles) of ethyl chloroacetate over a period of 2 hours with stirring at a temperature of no higher than -3°. The mixture was then stirred at -10 to -8° for a further 4 hours, left for 15 hours, and then boiled for 10-15 minutes until there was no longer an alkaline reaction to phenolphthalein; it was cooled to 30-40° and 610 ml of water added to dissolve the sodium chloride. The upper layer was separated, dried with baked potassium carbonate, and vacuum distilled with a fractionating column. An intermediate fraction with b.p. 55-58° at 10 mm was redistilled. The yield was 189.4 g, i.e., 55% of theoretical, calculated on the methyl n-propyl ketone; the b.p. was 88-93° at 10 mm.

2-Methylvaleraldehyde. Over a period of 1 hr 15 min, 172.2 g (1 mole) of ethyl β -methyl-β -n-propylglycidate was added with stirring to 126 ml of sodium hydroxide solution of specific gravity 1.285 (1.05 moles of NaOH), stirred and heated on a boiling water bath in a flask connected to a distillation condenser. After the addition, stirring and heating, accompanied by distillation of the alcohol, were continued for a further 6 hours; then the solution was cooled to 45° and 54 ml of sulfuric acid solution of specific gravity 1.540 added with stirring over a period of 10 minutes. The reaction mixture was left for 10 minutes and then decanted from the sodium sulfate precipitate.

The upper layer, containing the glycidic acid, was heated to 105° in a flask with a distillation condenser and then superheated steam passed through while the temperature in the reaction liquid was raised from 105 to 165° over a period of 1.5 hours and from 165 to 200° over 30 minutes. The 2-methyl-valeraldehyde distilled as it was formed. The oily layer, obtained in the distillate at a temperature above 165°, was redistilled and the fraction boiling at up to 125° in steam collected and added to the main mass. The layers present in the distillate were separated and their aldehyde contents determined. We obtained 83 g of 79.6% aldehyde and 178 g of aqueous layer, containing 0.8% aldehyde. The yield was 68 g, i.e., 68%, calculated on the ethyl β -methyl-β -n-propylglycidate. The 2-methylvaleraldehyde obtained was used in the synthesis of Meprotan without further purification.

SUMMARY

1. A method was developed for the preparation of 2-methylvaleraldehyde by decarboxylation of β -methyl-β -n-propylglycidic acid.

2. A convenient method was developed for the hydrolysis of ethyl β -methyl-β -n-propylglycidate..

3. The conditions for synthesizing ethyl β -methyl-β -n-propylglycidate by condensation of methyl n-propyl ketone with ethyl chloroacetate were determined more accurately.

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PREPARATION OF α,β'-LUTIDINE

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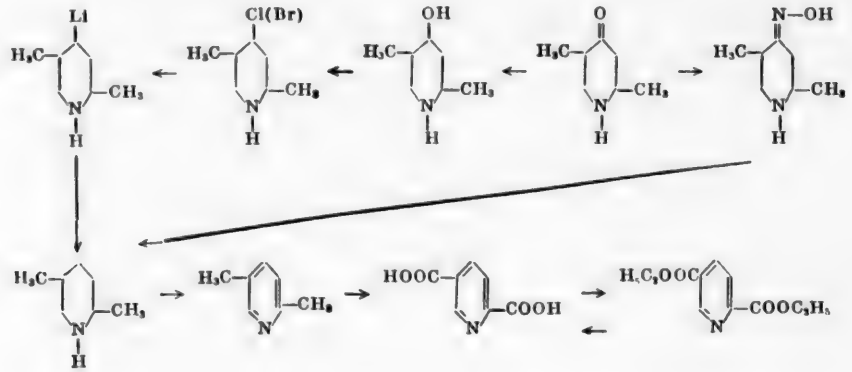
Like some other alkyl-(aryl- and alkenyl-) pyridines, α,β'-lutidine is a comparatively difficultly accessible substance. Considering the possibility of using certain substituted pyridines in the synthesis of some practically valuable products (starting materials for the preparation of polymeric materials, pharmaceutical preparations, etc.), we decided to study the method of preparing them from γ-piperidones. First of all we developed a method of synthesizing α,β'-lutidine from the accessible 2,5-dimethyl-4-piperidone [1, 2], which may be converted to 2,5-dimethylpiperidine in up to 40% yield by Kizhner reduction of its hydrazone or by decomposition of 2,5-dimethyl-4-lithiopiperidine with water. The latter is prepared by reduction of 2,5-dimethyl-4-piperidone to the corresponding piperidol, the hydroxyl group of this piperidine alcohol is replaced by halogen, and this is then replaced by lithium.



2,5-Dimethylpiperidine was converted into α,β'-lutidine catalytically. K-12 grade industrial dehydrogenation catalyst was used. It was established that piperidine was dehydrogenated to pyridine in 45% yield on this catalyst. 2,5-Dimethylpiperidine was dehydrogenated to α,β'-lutidine in 88% yield on the same catalyst. Oxidation of the α,β'-lutidine thus obtained gave isocinchomeronic acid, which was then converted to the diethyl ester.

EXPERIMENTAL

α,β'-Lutidine. 2,5-Dimethylpiperidine was dehydrogenated in a flow system over K-12 grade industrial dehydrogenation catalyst. Into the catalyst tube (made from quartz and the head was also quartz) was placed 50 ml of catalyst, which was activated in a stream of air at 400° over a period of two hours. The temperature in the catalyst zone during dehydrogenation was 390°. A stream of nitrogen was passed for 15 minutes and then 15.5 g of 2,5-dimethylpiperidine (b.p. 134-136° $n_D^{18.5}$ 1.4451), was passed at a constant rate over a period of 4.5 hours. We obtained 9750 ml of gas (p = 766 mm, t = 20°; H 99.4%, C_nH_{2n} 0.6%) and 13.8 g of condensate (a lemon-colored, mobile liquid, n_D^{19} 1.4975). Condensate (10.5 g) was distilled (in a stream of nitrogen):

1st fraction—b.p. 105-152°, 0.9 g, n_D^{19} 1.4700; 2nd fraction— α,β'- lutidine with b.p. 152-155°, 9.6 g, n_D^{19} 1.4999. From 1.4 g of the second fraction we obtained 3.9 g (after two recrystallizations from alcohol) of α,β'-lutidine picrate with m.p. 167-168°. The yield of α,β-lutidine was 88% (on the starting 2,5-dimethylpiperidine according to the catalyzate).

Piperidine was dehydrogenated on the same catalyst sample after similar activation. Over a period of 3.5 hours, 10 g of piperidine (b.p. 103-105°, $n_D^{16.5}$ 1.4560) was passed at a constant rate. The temperature in the catalyst zone was 365°. We obtained 3650 ml of gas (p = 732 mm, t = 20°; H 99.6%, CO_2 0.2% C_nH_{2n} 0.2%) and 9.3 g of catalyzate (n_D^{16} 1.5010). Distillation of the catalyzate yielded the following fractions of a mixture of pyridine and piperidine: 1st fraction—107-110°, 3.6 g, n_D^{17} 1.4748; 2nd fraction—110-115°, 0.8 g, n_D^{17} 1.4770; 3rd fraction—b.p. 115-125°, 1 g, n_D^{17} 1.4893. The residue after distillation weighed 2.8 g.

Isocinchomeronic acid and its diethyl ester. To a boiling solution of 33.5 g of potassium permanganate in 850 ml of water was added 5.6 g of the α,β'-lutidine described above. At first the reaction proceeded vigorously without heating and then for 7 hours with heating (gentle boiling). The manganese dioxide was separated by filtration and boiled three times with water (200 ml portions). The solution was evaporated to 500 ml under reduced pressure in a stream of carbon dioxide, neutralized with sulfuric acid (3.5 ml), and then evaporated to dryness. The residue was boiled with 100 ml of absolute alcohol. The insoluble residue (15.5 g) was collected by filtration. On cooling, the mother solution yielded 0.85 g of isocinchomeronic acid with m.p. 234-235°. The alcohol-insoluble residue, the residue after distillation of the alcohol from the mother solution remaining after separation of the acid, and 0.75 g of isocinchomeronic acid were boiled for 9 hours with 10 ml of sulfuric acid in 50 ml of absolute ethyl alcohol. The alcohol was removed in vacuum. To the residue was added 40 ml of water and then 5% aqueous potassium hydroxide solution (to litmus) in the presence of ether. When the ether extract had been dried with sodium sulfate, we obtained 3.5 g of a viscous liquid, which distilled over the range 70-130° at 1.5 mm and crystallized in the receiver. Recrystallization from ligroin yielded 2.3 g of diethyl isocinchomeronate with m.p. 42-44°.

Found % N 6.13, 6.32

$C_{11}H_{13}O_4N$. Calculated % N 6.28

Diethyl isocinchomeronate (1.6 g) was boiled with 11 ml of 10% aqueous potassium hydroxide solution. The solution was neutralized with dilute sulfuric acid (0.5 ml of concentrated sulfuric acid and 10 ml of water) and evaporated to dryness in vacuum. The residue (2.6 g) was boiled with 15 ml of absolute alcohol and then filtered rapidly. On cooling, the mother solution yielded 0.55 g of isocinchomeronic acid with m.p. 234-235°.

SUMMARY

Catalytic dehydrogenation of 2,5-dimethylpiperidine gave a quantitative yield of α,β-lutidine.

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PREPARATION OF PYRIDINECARBOXYLIC ACIDS

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Until recently the best results in preparing pyridinecarboxylic acids, in particular, nicotinic and isonicotinic acids, have been obtained by liquid-phase oxidation of β- and γ-substituted pyridines with potassium permanganate [1], and nitric [2] and sulfuric acids [3, 4].

In the period 1944-1948 reports were published on the preparation of nicotinic acid by gas-phase oxidation of β-picoline with atmospheric oxygen in the presence of catalysts [5, 6] but these methods have not found wide application. In 1952 it was found that oxidation of β- and γ-picolines with atmospheric oxygen mixed with ammonia in the presence of catalysts gave nicotino- and isonicotinonitriles [7].

In this work we describe the preparation of β'- and γ-pyridinecarbonitriles by the action of atmospheric oxygen in the presence of ammonia and vanadium pentoxide, deposited on aluminum oxide. Conversion of the nitriles synthesized to acids and then to esters of β'- and γ-pyridinecarboxylic acids, followed by treatment of the latter with ammonia gave nicotinamide and isonicotinamide. The low yield in the conversion of the nitriles to amides through the acids and esters compelled us to use another method for preparing the amides—treatment of the nitriles obtained with hydrogen peroxide in an alkaline medium.

EXPERIMENTAL

Preparation of catalyst. To 50 g of ammonium metavanadate in 500 ml of distilled water was added 50 g of aluminum oxide (particles 2-3 mm across) and the water evaporated. The mass obtained was dried at 100-110° and fired in a stream of air at 400° for 10-12 hours.

Preparation of β- and γ-pyridinecarboxylic acids from β'- and γ-picolines. The individual β'- and γ-picolines were oxidized to β'- and γ-pyridinecarbonitriles in the following way: Air, dried in a column with calcium chloride and a bottle with sulfuric acid, was passed into an evaporator where it was saturated with the vapor of β- (b.p. 142°) and γ-picoline (b.p. 144°). The air flow was kept at 0.6 liter/min and the evaporator temperature at 35°; under these conditions β-picoline evaporated at 0.788 g/hour and γ-picoline at 0.68 g/hour.

The air, saturated with the picoline vapor, was passed into a heater, where it was mixed with ammonia, supplied from a tank through a rheometer at 0.5 liter/min., and then into a quartz tube, filled with 20 cc of vanadium catalyst and heated to 320-340°. The crystalline β- and γ-pyridinecarbonitriles obtained passed through a condenser into a receiver with water; then to an aqueous ammonia solution, containing 0.8 g of γ-pyridinecarbonitrile, was added 30 g of barium hydroxide, the mixture boiled under reflux until the evolution of ammonia ceased and neutralized to pH 2-3 with dilute (1 : 1) sulfuric acid, and the barium sulfate separated. The filtrate was evaporated to 50-60 ml in vacuum (15-20 mm) and cooled to -5 to -1°. The precipitated γ-pyridinecarboxylic acid was separated and dried at 80-90°. The yield was 0.85 g, 19.31% on γ-picoline; m.p. 313-315° (from water). β-Pyridinecarboxylic acid was obtained similarly. The yield was 35% on β-picoline; m.p. 234-236° (from water).

Preparation of β-pyridinecarbonamide. To an aqueous ammonia solution, containing 1.96 g of β-pyridinecarbonitrile, heated to 42°, was added 4.5 g of potassium hydroxide and 15 ml of 30% hydrogen peroxide. The mixture was stirred for an hour, neutralized with ammonium chloride (4.45g), and boiled under reflux until the

evolution of ammonia ceased. The solution was evaporated in vacuum (15-20 mm). The residue was extracted with ethyl acetate. The combined extracts were concentrated and the crude product which precipitated was recrystallized from ethyl acetate and dried in vacuum (8-10 mm) at 50-60°. The yield (1.5 g) was 36.5% on β-picoline; m.p. 122-125° (from ethyl acetate).

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METHOD OF PREPARING 1, 4-DICHLOROBUTANE FROM TETRAHYDROFURAN

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In a previous communication we demonstrated the possibility of preparing 1, 4-dichlorobutane and 4,4'-dichlorodibutyl ether from tetrahydrofuran and phosgene. The processes were carried out both in batches and continuously [1]. In the present work we describe a method of preparing 1,4-dichlorobutane by treating tetrahydrofuran with gaseous HCl at an elevated temperature and normal pressure in the presence of $ZnCl_2$ as catalyst. The process was carried out both in batches and continuously.

EXPERIMENTAL

Batch method of preparing 1,4-dichlorobutane. Into a four-necked flask, fitted with a stirrer, reflux condenser, thermometer, and bubbler, were placed 72 g (1 mole) of tetrahydrofuran and 18 g of anhydrous $ZnCl_2$, and 3 moles of gaseous HCl was passed through the bubbler at 60-70°. As the reaction products were formed, the temperature of the reaction mixture was gradually raised to 120°. The duration of the reaction was 12 hours. After cooling, the reaction products were washed with water until neutral to Congo, dried, and fractionated in vacuum. Two fractions were obtained at 13 mm: 1) b.p. 48-50° (94 g), corresponding to 1,4-dichlorobutane in 74% yield, calculated on tetrahydrofuran; 2) b.p. 126-128° (14.5 g), corresponding to 4,4'-dichlorodibutyl ether in a yield of 14.6% of theoretical.

The continuous method was accomplished in a large-scale laboratory apparatus consisting of a reactor, which was a vertical tube of the material ATM-1 (acid-resistant and having a high thermal conductivity), 1500 mm in length, 48 mm in external diameter, and 36 mm in internal diameter, filled with 1425 ml of packing, 2-3 mm in size (crushed porcelain Raschig rings), connected to two receivers in series, a condenser, and a wash bottle to remove unreacted hydrogen chloride. The reaction tube was heated with a heat-transfer fluid, consisting of a mixture of diethylene glycol and water with a boiling point of 107-108°, with the aid of an external boiler. This form of heating ensured a uniform temperature throughout the reactor. The temperature was measured with a technical thermometer inside the reactor.

The process was carried out in the following way: Tetrahydrofuran with $ZnCl_2$ dissolved in it (complete solution of the zinc chloride could only be achieved by passing a small amount of hydrogen chloride through the mixture) was introduced into the reacter at the top from a dropping funnel. At the same time a stream of dry hydrogen chloride was passed into the reactor through a rheometer. The product was collected in a receiver underneath the reactor, and the excess hydrogen chloride was trapped in water.

Example. Through the reactor was passed 432 g (6 moles) of terrahydrofuran, 144 g (0.176 mole or 33% of the weight of tetrahydrofuran) of $ZnCl_2$, and 295.8 liters (481.8 g or 13.2 moles) of HCl.

Operating conditions: the rate of tetrahydrofuran input was 150 ml/hour, the rate of HCl input 90-95 ml/hour, the reaction temperature 105°, and the space velocity 0.1.

The reaction products were treated as in the batch process.

Distillation at 13 mm yielded two fractions: 1) b.p. 48-50° (600 g), corresponding to 1.4-dichlorobutane; 78.7% yield, calculated on tetrahydrofuran; 2) b.p. 126-128° (27 g), corresponding to 4,4'-dichlorodibutyl ether in a yield of 4.5% of theoretical.

By reaction with hydrogen chloride in the presence of zinc chloride, 4,4'-dichlorodibutyl ether may be completely converted into 1,4-dichlorobutane.

1,4-Dichlorobutane is a colorless, mobile liquid which is insoluble in water but readily soluble in the usual organic solvents; it has b.p. 48-50°, d_4^{20} 1.1283, n_D^{20} 1.4520.

4,4'-Dichlorodibutyl ether is a slightly yellowish liquid which is insoluble in water but soluble in the usual organic solvents; it has b.p. 126-128°, d_4^{20} 1.0747, n_D^{20} 1.4568.

SUMMARY

We developed batch and continuous methods of preparing 1,4-dichlorobutane from tetrahydrofuran and gaseous hydrogen chloride in the presence of zinc chloride at normal pressure and an elevated temperature to give good yields of product.

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SYNTHESIS OF BENZNAPHTHONE FROM β-NAPHTHOL

S. M. Shein

Benznaphthone, which is the starting material for the synthesis of some vat dyes and acetate silk dyes [1-3] is prepared by several methods [4-22].

The most widely used method of preparing benznaphthone is the reaction of α- or β-naphthol with glycerol in concentrated sulfuric acid [4-9] or in anhydrous hydrogen fluoride [10, 11].

For the reaction in sulfuric acid, m-nitrobenzenesulfonic acid [5-8] and pyroarsenic acid [9] are used as oxidants, and manganese acetate and vanadic acid [5] have been proposed as catalysts.

According to patent data [5], condensation of β-naphthol with glycerol in 68% sulfuric acid gave a 32-36% yield of benznaphthone. Using the material in this patent, Zil'berman and Barkov [6] obtained a 50% yield of benznaphthone, Lukin [8] obtained 55%, while Fieser and Hershberg [7] obtained only 26%.

The use of pyroarsenic acid as oxidant gave a benznaphthone yield of 10-12% [9].

Isolation of the product in an acid medium gave a tarry substance and poor results were obtained when the benznaphthone was subsequently extracted with ether [5-7]. This could be avoided by adding the filtered solution of benznaphthone in sulfuric acid to a dilute alkali solution at low temperature [8]. On synthesizing benznaphthone according to data in patent [5] we obtained the product in 10 to 36% yields.

We carried out a comparative investigation of ammonium vanadate, hydrated ferrous sulfate, and ferric sulfate as catalysts. The best results were obtained with hydrated ferrous sulfate.

Data on the effect of catalysts on the benznaphthone yield (H_2SO_4 concentration 70% and 14 moles of H_2SO_4 per mole of β-naphthol) are given in Table 1.

The effect of the amount and concentration of sulfuric acid was studied (Table 2). The best benznaphthone yield (46-48%) was obtained with 70% sulfuric acid with 14-15 moles of the latter per mole of β-naphthol and hydrated ferrous sulfate as catalyst.

TABLE 1

Catalyst	Without catalyst	NH_4VO_4	$Fe_2SO_4 \cdot 6H_2O$	$Fe_2(SO_4)_3$
Yield (in %)	29	to 36	46-48	34.38

EXPERIMENTAL

Benznaphthone. A mixture of 700 g of 70% sulfuric acid, 50 g of β-naphthol, 15 g of hydrated ferrous sulfate, and 90 g of glycerol was heated to 110° and 27 g of sodium m-nitrobenzenesulfonate added over a period of 15 minutes. The reaction mixture was heated to 138°, kept at this temperature for 30-40 minutes, and cooled to room temperature. The solution was filtered to remove the precipitate and poured into a mixture of 100 g of

TABLE 2

Effect of Amount and Concentration of H_2SO_4 on Benznaphthone Yield

	No. of moles of H_2SO_4 (70%) per mole of β-naphthol			H_2SO_4 concentration (14 moles per mole of β-naphthol)			
	6.8	10.2	14.8	68%	70%	72%	75%
Yield (in %)	21	48	46—48	41—43	46—48	22	36
Melting point (in °C)	147—148	130—131	146—147	146—147	146—147	136—137	130—133

40% sodium hydroxide solution and 3000 g of ice at a temperature no higher than 5°. The benznaphthone precipitate was collected, washed with water, and dried at 50°. The yield was 31.2 g or 47.5%. The product contained 5% of iron hydroxide and had m.p. 146-147°; after recrystallization from alcohol, it had m.p. 152-153°. According to literature data the m.p. is 150°[10], 151°[11], 152-153° [4, 6, 8] and 153-154° [5, 15].

A typical experiment is described above. Not less than 2-3 experiments were carried out in parallel.

SUMMARY

It was shown that the reaction of β-naphthol with glycerol (m-nitrobenzenesulfonic acid as oxidant) gave the optimal yields (46-48%) of benznaphthone in 70% sulfuric acid with 14-15 moles of acid per mole of β-naphthol. Hydrated ferrous sulfate is proposed as a catalyst for this reaction.

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SYNTHESIS OF ACID AND MIXED ESTERS OF ADIPIC ACID

N. V. Komarov and I. L. Kotlyarevskii

Most of the neutral esters of dibasic acids have good lubricating properties. In this connection, diesters of dibasic acids have been used as special low-temperature lubricants. A number of articles and patents [1-10] have been devoted to this problem, and they indicate that branched and unsymmetrical diesters and also mixtures of various diesters have the best lubricating properties.

The purpose of this work was to synthesize a mixed diester with a branched radical. The diester we chose was cyclohexyl 2-ethylhexyl adipate.

This diester was synthesized from adipic acid and the appropriate alcohols by the following scheme:

$$C_6H_{11}OH + HOCO(CH_2)_4COOH \rightarrow C_6H_{11}OOC(CH_2)_4COOH$$

$$C_6H_{11}OOC(CH_2)_4COOH + C_4H_9{-}\underset{\displaystyle C_2H_5}{\underset{|}{C}}HCH_2OH \rightarrow C_6H_{11}OOC(CH_2)_4COOCH_2{-}\underset{\displaystyle C_2H_5}{\underset{|}{C}}HC_4H_9$$

i.e., through the formation of the acid cyclohexyl ester of adipic acid. It should be noted that there are very limited data on the synthesis of acid esters of adipic acid based on the reaction of the latter with alcohols.

The literature contains mainly patent data [4-9], which do not include synthesis conditions. In 1952 Titov and Matveeva [10, 11] investigated the reaction of cyclohexanol with adipic acid and attempted to isolate monohexyl adipate, but were unsuccessful. We obtained this ester in 80.7% yield by reacting cyclohexanol directly with excess adipic acid without catalysts. Reaction of the acid cyclohexyl ester of adipic acid with 2-ethylhexyl alcohol gave a good yield of cyclohexyl 2-ethylhexyl adipate. In order to prove the structure of the mixed ester obtained and find another way of synthesizing this ester, we also obtained the latter by another scheme:

$$C_4H_9\underset{\displaystyle C_2H_5}{\underset{|}{C}}HCH_2OH + HOOC(CH_2)_4COOH \rightarrow C_4H_9\underset{\displaystyle C_2H_5}{\underset{|}{C}}HCH_2OOC(CH_2)_4COOH$$

$$C_4H_9\underset{\displaystyle C_2H_5}{\underset{|}{C}}HCH_2OOC(CH_2)_4COOH + C_6H_{11}OH \rightarrow C_4H_9\underset{\displaystyle C_2H_5}{\underset{|}{C}}HCH_2OOC(CH_2)_4COOC_6H_{11}$$

i.e., through the formation of mono-2-ethylhexyl adipate. The acid esters of adipic acid prepared were colorless, water-insoluble liquids. When stored for a long time and when heated they decomposed to give adipic acid. During extraction of these esters from the reaction mixture with a 5% aqueous solution of sodium hydroxide, followed by treatment of the alkaline extracts with dilute hydrochloric acid, the esters were very readily hydrolyzed to the original alcohol and adipic acid. Mono-2-ethylhexyl adipate was hydrolyzed more readily than monocyclohexyl adipate. In this connection, freezing and rapid vacuum distillation were used to isolate the acid esters of adipic acid. According to alkali titration, the esters prepared were 98-99% pure.

On comparing the two methods given above for the synthesis of cyclohexyl 2-ethylhexyl adipate, it was found that the most convenient one was the first synthesis, i.e., through the formation of monocyclohexyl adipate. Cyclohexyl 2-ethylhexyl adipate is a colorless liquid with a freezing point below -65°. In contrast to acid esters, this ester is very stable and burned extremely slowly during elementary analysis.

EXPERIMENTAL

The following starting materials were used for the synthesis of esters: adipic acid with m.p. 152°; cyclohexanol with b.p. 160°, n_D^{25} 1.4657, d_4^{25} 0.9615; 2-ethylhexyl alcohol with b.p. 184°, n_D^{20} 1.4300, d_4^{20} 0 8332.

Synthesis of monocyclohexyl adipate. Into a 0.5-liter round-bottomed flask, fitted with a thermometer, dropping funnel, reflux condenser, and modified Dean and Stark head, was placed 146 g (1 mole) of adipic acid. The flask was heated until all the adipic acid melted. Then 50 g (0.5 mole) of cyclohexanol was added dropwise. Water, formed during the reaction, collected in the receiver of the head. The end of the reaction was marked by the separation of the theoretical amount of water. For completion of the reaction after the addition of all the cyclohexanol, the mixture was usually heated for a further 1-2 hours at 140-150°. At the end of the reaction, the mixture was cooled and transferred to a Buchner funnel, where the excess adipic acid was separated by filtration and washed with ether. The ether solution obtained by washing the precipitate was transferred to a distillation flask, where the ether was removed by distillation. The residue was combined with the filtrate and twice cooled to - 15°. We isolated 75 g of adipic acid and 101 g of crude monocyclohexyl adipate, which was rapidly vacuum distilled. We isolated 92 g of material with b.p. 170-171° (1.5 mm Hg) and n_D^{20} 1.4687, d_4^{20} 1.0697; the yield was 80.7%.

Found %: C 63.83, 63.91; H 8.62, 8.81, MR_D 59.4.

$C_{12}H_{20}O_4$. Calculated %: C 63.13, H 8.83; MR_D 58.9

The synthesis of 2-ethylhexyl adipate was carried out in the same apparatus and by a method analogous to that described above. From 146 g (1 mole) of adipic acid and 65 g (0.5 mole) of 2-ethylhexyl alcohol we isolated 97 g (75.2%) of substance with b.p. 167° (1 mm Hg), n_D^{20} 1.4497, d_4^{20} 0.9897.

Found %: C 65.41, 65.31; H 10.23, 10.05; MR_D 70.25.

$C_{14}H_{26}O_4$. Calculated %: C 65.07; H 10.14; MR_D 70.27.

Synthesis of cyclohexyl 2-ethylhexyl adipate. 1. Into the apparatus described above was placed a mixture of 176 g (0.77 mole) of monocyclohexyl adipate and 100 g (0.77 mole) of 2-ethylhexyl alcohol. The mixture was heated until the theoretical amount of water had been liberated, dried with sodium sulfate, and vacuum distilled. We isolated 239 g (91%) of a substance with b.p. 174-175° (1 mm Hg), n_D^{20} 1.4592, d^{20}_4 0.9807.

Found %: C 69.22, 68.97; H 10.37, 10.25; MR_D 96.14.

$C_{20}H_{36}O_4$. Calculated %: C 70.54, H 10.65; MR_D 96.17.

The C and H analyses are low due to the difficulty of burning the substance.

2. The synthesis was carried out analogously to the previous one. In it we used 91 g (0.35 mole) of mono-2-ethylhexyl adipate and 35 g (0.35 mole) of cyclohexanol. As a result we obtained 103.5 g (87%) of cyclohexyl 2-ethylhexyl adipate with the same constants.

SUMMARY

1. Using as examples the reactions of adipic acid with cyclohexanol and 2-ethylhexyl alcohol, we developed a simple method of synthesizing acid esters of adipic acid.

2. The possibility of synthesizing mixed esters of adipic acid was demonstrated by the reaction of monoesters of this acid with cyclohexanol and 2-ethylhexyl alcohol.

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Akhumov, E. I. - 1259
Akim, L. E. - 1356
Akimova, M. P. - 638
Akopyan, A. E. - 241
Akopyan, A. E. - 1625
Alabyshev, A. F. - 66
Alekseeva, A. N. - 1477
Alekseeva, L. A. - 2881
Aleskovskii, V. B. - 1575
Al'tshuler, O. V. - 1457
Altykis, A. I. - 628
Amirova, S. A. - 1519
Andreev, D. N. - 2888
Andreeva, G. A. - 2400
Andreeva, G. P. - 2287
Andreeva, I. V. - 1893
Andreeva, L. F. - 2430
Andreeva, M. I. - 1702
Andreeva, M. I. - 1952
Andrianov, K. A. - 203
Andrianov, K. A. - 488
Andrianov, K. A. - 900
Andrianov, K. A. - 1376
Andrianov, K. A. - 1652
Andrianov, K. A. - 2385
Andrianov, K. A. - 2759
Angert, L. G. - 427
Anisimov, K. N. - 181
Anisimov, K. N. - 372
Anisimov, K. N. - 685
Anpilova, N. S. - 1264
Antipenko, G. L. - 1498
Antipenko, G. L. - 1760
Antipina, A. A. - 481
Antonova, E. A. - 2536
Antonovskii, S. D. - 720
Appen, A. A. - 991
Appen, A. A. - 1006
Appen, A. A. - 1239
Appen, A. A. - 2536
Appen, A. A. - 2652
Arbuzova, I. A. - 2310
Archakov, Yu. I. - 2745
Aronson, Yu. P. - 1444
Atroshchenko, V. I. - 100
Atroshchenko, V. I. - 1020
Averbukh, B. D. - 1255
Averbukh, Ya. D. - 820
Avgustinik, A. I. - 1177
Avgustinik, A. I. - 1481
Avgustinik, A. I. - 1487
Avgustinik, A. I. - 1715
Avgustinik, A. I. - 2409
Avgustinik, A. I. - 2864
Azelitskaya, R. D. - 1215

Babanov, B. M. - 810
Babkin, A. G. - 1702
Babkin, A. G. - 1952
Babkin, Yu. A. - 1195
Baburina, A. N. - 1832
Baburina, A. N. - 1918
Babushkin, V. I. - 45
Badmas, T. G. - 1356
Bakk, L. A. - 1259
Balandin, A. A. - 1630
Balandin, A. A. - 2640
Balandin, I. M. - 1195
Balandina, O. B. - 1051
Balashova, I. M. - 167
Balezin, S. A. - 1094
Balezin, S. A. - 1685
Ban'shchikova, T. A. - 963
Barannikov, G. I. - 749
Baranov, S. N. - 2679
Baratov, A. N. - 1181
Barchuk, V. T. - 859
Bardyshev, I. I. - 2634
Barmashenko, I. B. - 845
Baskakov, Yu. A. - 1446
Baralin, O. E. - 2800
Baulina, G. A. - 2906
Beletskaya, E. S. - 1498
Beletskaya, E. S. - 1760
Belitskaya, R. M. - 398
Belonovskaya, G. P. - 1863
Belyaev, P. P. - 2089
Berdyanskaya, R. A. - 1978
Berezin, I. V. - 175
Berezin, I. V. - 906
Berg, L. G. - 2649
Bergman, A. G. - 534
Bergman, A. G. - 742
Berkman, Ya. P. - 1245
Berkman, Ya. P. - 2734
Berlin, A. A. - 880
Berlin, A. A. - 1606
Berlin, A. A. - 2304
Berman, I. D. - 826
Bernshtein, A. V. - 457
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Bespalova, L. L. - 2624
Bespalova, L. L. - 2820
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Bezuglyi, D. V. - 273
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Bibr, B. - 1020
Blinov, V. A. - 693
Blinov, V. A. - 1595
Blinova, M. V. - 2847
Bogatina, K. G. - 284
Bogatyreva, E. V. - 1094
Bogdanov, M. I. - 632
Bogomolov, B. N. - 2192
Bogoslovskii, B. M. - 2278
Bogoslovskii, V. N. - 1184
Bol'shakov, A. G. - 95
Bol'shakov, A. G. - 792
Bol'shakov, A. G. - 1904
Bol'shakov, A. G. - 2037
Bondarchuk, T. P. - 1324
Borisikhina, V. I. - 1189
Borisikhina, V. I. - 2012
Borisov, S. N. - 2428
Bork, V. A. - 774
Bork, V. A. - 1493
Borodkina, L. I. - 291
Borodkina, L. I. - 2660
Borok, B. A. - 1413
Borok, B. A. - 1646
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Borzova, I. - 473
Borzova, L. D. - 2437
Boyadzhiev, L. - 2080
Brainina, Kh. Z. - 2697
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Burshtein, R. Kh. - 2299
Buryakovskaya, R. I. - 481
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Bushmakin, I. N. - 1306
Bushmakin, I. N. - 1787
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Chen, N. G. - 1287
Chen, N. G. - 1553
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Chepelevetskii, M. L. - 970
Cherkasov, N. Kh. - 2002
Chekmareva, I. B. - 2906
Chernyak, A. S. - 2201
Chertkov, B. A. - 78
Chertkov, B. A. - 975
Chertkov, B. A. - 983
Chertkov, B. A. - 1417
Chertkov, B. A. - 1732
Chertkov, B. A. - 1743
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Chertkov, B. A. - 2687
Chertkov, Ya. B. - 378
Chervinskaya, O. V. - 1264
Chirikova, A. V. - 689
Chizhikov, D. M. - 1252
Chochieva, M. M. - 643
Chudakov, M. I. - 638
Chufarov, G. I. - 1184
Chufarov, G. I. - 1255
Chü Fu-fu - 571
Chumakov, S. Ya. - 1173
Daniel'-Bek, V. S. - 679
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Dashevskii, M. M. - 2285
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Davankov, A. B. - 753
Davankov, A. B. - 2321
Davydov, A. T. - 2028
Davydov, V. I. - 462
Davydova, V. P. - 1130
Degteva, T. G. - 398
Deich, A. Ya. - 1907
Delimarskii, Yu. K. - 607
Denisov, E. T. - 906
Derevyankin, V. A. - 2449
Deryagin, B. V. - 2759
Dezheni, D. - 2614
Diev, N. P. - 462
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Dobrolyubov, V. V. - 2556
Dobromil'skaya, I. M. - 195
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Dodonov, Ya. Ya. - 2437
Dogadkin, B. A. - 910
Dokunikhin, N. S. - 693
Dokunikhin, N. S. - 1595
Dolgoplosk, B. A. - 1863
Dolgopol'skii, I. M. - 195
Dolgov, B. N. - 2142
Dombrovskaya, N. S. - 2886
Donev, L. - 2080
Drinberg, A. Ya. - 1380
Drinberg, A. Ya. - 2126
Drozdov, B. V. - 1579
Dubrovin, G. I. - 2620
Dubrovnik, R. I. - 2314
Dubrovo, S. K. - 767
Dubrovo, S. K. - 1001
Dubrovo, S. K. - 1232
Dudkin, M. S. - 1930
Dudkin, M. S. - 2403
Dukhankina, L. S. - 841
D'yakova, M. K. - 2172
Dyatlova, V. P. - 50
Dybina, P. V. - 1747
Dykhanov, N. N. - 941
Dykhanova, A. S. - 941
Dzhenchel'skaya, S. - 1376

Edlinskii, Z. I. - 1198
Egorova, E. N. - 1973
Éidus, Ya. R. - 422
Éidus, Ya. T. - 442
Éidus, Ya. T. - 1857
Éitingon, I. I. - 910
Ekaterinina, L. N. - 487
Ekaterinina, L. N. - 926
El'kin, B. I. - 1899
Émanuél', N. M. - 175
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Émdina, R. Ya. - 2883
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Englin, B. A. - 2810
Enikolopyan, N. S. - 930
Enikolopyan, N. S. - 1156
Epel'baum, V. A. - 1990
Eppel', F. A. - 1850
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Erekaev, V. P. - 244
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Esin, O. A. - 325
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Étlis, V. S. - 1676
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Fedot'ev, N. P. - 1575
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Fedot'ev, N. P. - 2566
Fedot'ev, N. P. - 2876
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Fel'desh, P. - 2263
Fel'dshtein, M. S. - 910
Filatov, I. G. - 2433
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Filimonov, B. F. - 1926
Finkel'shtein, A. I. - 2148
Flerov, V. N. - 133
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Flid, R. M. - 238
Flid, R. M. - 689
Flis, I. E. - 295
Fomina, E. A. - 2697
Forst, A. M. - 1380
Frantsevich, T. F. - 859
Freidin, B. G. - 1888
Friedlin, L. Kh. - 918
Freidlin, L. Kh. - 1630
Frenkel, Ya. P. - 2334
Fridman, I. D. - 1962
Fridman, V. M. - 864
Frolov, A. F. - 2120
Fundyler, B. M. - 1380
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Galenko, N. P. - 359
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Galkin, A. F. - 2906
Galkina, N. I. - 2299
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Gamazov, V. P. - 1543
Gamzulov, Ya. I. - 105
Ganelina, S. G. - 2649
Gan'Fu-hsi(Kan Fu-hsi) - 991
Gan'Fu-hsi(Kan Fu-hsi) - 1006
Gan'Fu-hsi(Kan Fu-hsi) - 1013
Gan'Fu-hsi (Kan Fu-hsi) - 1239
Gan'Fu-hsi (Kan Fu-hsi) - 2652
Ganz, S. N. - 992
Ganz, S. N. - 998

Ganz, S. N. - 1512
Ganz, S. N. - 2259
Gaponenkov, T. K. - 491
Garmanova, E. N. - 2662
Gasyuk, G. N. - 95
Gasyuk, G. N. - 792
Gasyuk, G. N. - 1904
Gasyuk, G. N. - 2037
Gavrya, N. A. - 100
Gavurina, R. K. - 873
Gavurina, R. K. - 1086
Gavurina, R. K. - 1109
Gel'd, P. V. - 86
Gel'shtein, R. M. - 1204
Gel'perin, N. I. - 628
Gel'perin, N. I. - 2050
Genes, R. G. - 1420
Genes, R. G. - 1915
Gerchuk, M. P. - 244
Gimaddinov, Zh. K. - 1923
Ginberg, A. M. - 591
Gintsberg, S. A. - 484
Ginstling, A. M. - 2223
Gitman, E. B. - 607
Gleim, V. G. - 222
Gleim, V. G. - 799
Gleim, V. G. - 1069
Glushkov, R. G. - 937
Glushkova, M. A. - 1947
Goftman, M. V. - 922
Gogol', V. - 473
Gol'dberg, N. A. - 2898
Gol'dfarb, Ya. L. - 427
Golendeev, V. P. - 2665
Golomb, L. M. - 1873
Goloushin, N. S. - 2016
Golovchinskaya, E. S. - 937
Golubtsov, S. A. - 203
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Golyand, S. M. - 1978
Gorbman, S. I. - 992
Gorbman, S. I. - 998
Gorelik, G. N. - 1380
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Goroshchenko, Ya. G. - 1952
Gorshkov, V. S. - 20
Gorushkina, G. I. - 427
Goryaev, M. I. - 1923
Goryaev, M. I. - 2364
Govorkov, V. M. - 820
Grachev, K. Ya. - 216
Grakhova, S. G. - 1137
Granova, Z. A. - 873
Granovskii, Yu. V. - 2644
Grigor'eva, A. G. - 2520
Grigor'eva, N. K. - 2237
Grigorovskii, A. M. - 1845
Grilikhes, S. Ya. - 1191
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Grin, Yu. D. - 855
Grinina, V. V. - 2001
Grishanina, N. P. - 1130
Grishchuk, A. P. - 2679
Gritsan, D. N. - 1436
Grobov, I. N. - 891
Gubanov, É. F. - 2649
Gudkov, S. F. - 354
Gurevich, B. S. - 659
Gurevich, M. A. - 1990
Gurovich, E. I. - 836
Gurovich, E. I. - 2751
Gurvich, S. M. - 1676
Gus'kov, V. M. - 1405
Gyunner, E. A. - 1910
Ignatova, N. P. - 2629
Il'ina, D. E. - 1439
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Ioanesova, A. L. - 2836
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Ivanova, E. A. - 1469
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Kagarlitskii, A. D. - 404
Kalinkin, S. F. - 2406
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Kalyuzhnyi, V. M. - 2599
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Karpinskii, M. N. - 2393
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Kasatkina, N. G. - 171
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Kataev, G. A. - 2520
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Khan, O. A. - 841
Kharakhorin, F. F. - 1457
Kharkharov, A. A. - 1601
Kharlamov, I. P. - 465
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Khonikevich, A. A. - 2566
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Kireeva, M. V. - 528
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Klebanskii, A. L. - 2114
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Klopov, B. N. - 2810
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Kossyi, G. G. - 1433
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Krushinskaya, E. P. - 632
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Legkun, Ya. A. - 1592
Leibovich, S. B. - 992
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Leitman, Ya. I. - 1881
Leitman, Ya. I. - 2830
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Lesina, K. P. - 2304
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Levin, A. I. - 1825
Levin, P. A. - 2422
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Libina, R. I. - 2702
Likhterov, V. R. - 1676

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Lokshin, M. A. - 2259
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Molotkova, E. N. - 2572
Morachevskii, A. G. - 483
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Morachevskii, Yu. V. - 1973
Morgart, R. M. - 851
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Murach, N. N. - 584
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Musatova, L. V. - 1643
Muzyka, I. D. - 1985
Myagkova, A. R. - 1352

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Nadinskaya, O. V. - 1766
Nadinskaya, O. V. - 1901
Nalbandyan, A. B. - 930
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Ostroumov, V. V. - 330
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Pechkovskii, V. V. - 1519
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Romanova D.L. - 1575
Romanova T.G. - 864
Rominyan, A. L. - 2755
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Rostovskii, E. N. - 2001
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Rybakova, N. A. - 880
Rybakova, N. A. - 1606
Rylov, V. S. - 1400

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Semenov, G. A. - 1536
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Semushin, A. M. - 2245
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Sergeenkova, K. K. - 1662
Sergeev, V. V. - 1708
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Sevast'yanov, N. G. - 1990
Shabalin, K. N. - 1506
Shabanov, I. M. - 2364
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Sharf, V. Z. - 918
Sharkov, V. I. - 2417
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Shostak, F. T. - 1272
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Shpunt, A. Ya. - 1994
Shreider, A. V. - 1346
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Shteinberg, B. Sh. - 2097
Shtokman, G. P. - 2751
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Shukalova, E. A. - 1099
Shun, D. S. - 1436
Shur, A. M. - 1926
Shur, B. F. - 1926
Shvekhgeimer, G. A. - 1209
Sidel'nikova, G. I. - 2152
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Suchkov, A. B. - 1413
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Sumarokov, V. P. - 2594
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Teodorovich, V. P. - 2457
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Vladyrchik, O. S. - 2624
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Vlasova, V. M. - 1115
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Vol'-Épshtein, A. B. - 2172
Vol'fkovich, S. I. - 963
Volkhonskii, N. V. - 1575
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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

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